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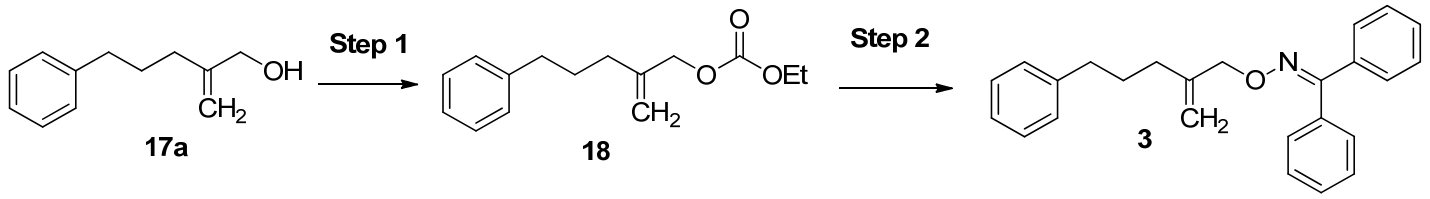
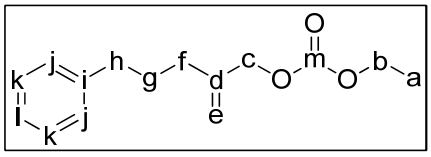
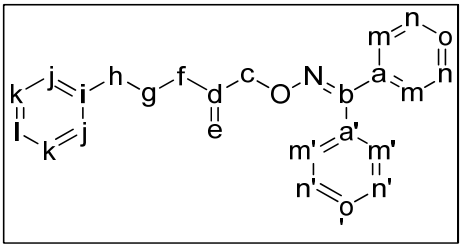
General information

Reactions were carried out in a dry nitrogen atmosphere. Tetrahydrofuran (THF) was freshly distilled under sodium metal and benzophenone. HPLC solvents were filtered through Millipore filter paper. 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (pinBH) was distilled immediately before usage. All synthesized compounds were purified with flash chromatography using EMD Silica Gel 60 Geduran®. Thin Layer Chromatography analyses were performed on Analtech Silica Gel HLF (0.25 mm) precoated analytical plates and visualized with use of handheld short wavelength UV light, iodine stain (I_2 and EMD Silica Gel 60 Geduran®) and vanillin stain (EtOH, H_2SO_4, and vanillin). HPLC analyses were performed with use of an ISCO model 2360 HPLC and Chiral Technologies, Inc. chiral HPLC columns (Chiralcel-OD, Chiralpak-AD, -IB and -IC columns: 250 x 4.6 mm) fitted with Chiralpak-AD (50 x 4.6 mm) as a guard (except Chiralpak-IC which was used without guard) and monitored with UV-VIS detector (Shimadzu SPD-$10A_{VP}$/$10A_{VP}$, λ = 210 nm). HPLC samples were prepared using indicated eluent mixture as a solvent. GC analyses were performed with use of J&W Scientific ID Cyclosil β (30 m x 0.25 mm x 0.25μm) and Varian CP-Chirasil-DEX CB (25 m x 0.32 mm x 0.25μm) capillary columns with FID detector. Data were recorded and analyzed with ChromPerfect chromatography software (version 5.1.0). NMR spectra were recorded on 700, 400, and 300 MHz Bruker Advance NMR spectrometers using residue $CHCl_3$ (δ 7.27 ppm for ^{1}H NMR) or $CDCl_3$ (δ 77.16 ppm for ^{13}C NMR) for reference unless otherwise specified. Peaks are expressed as m (unresolved multiplet), quin (quintet), q (quartet), t (triplet), d (doublet), s (singlet), br s (broad singlet), dd (doublet of doublets), etc. IR spectra were recorded using an Avatar 360 FT-IR. Optical rotations were measured as solutions 1.0 g/100 mL (c = 1.0) in chloroform, acetone or ethanol unless indicated otherwise, and recorded using an Autopol III automatic polarimeter. Specific rotation values are reported in units of deg $dm^{-1}cm^3g^{-1}$. ESI-HRMS analyses were performed by the Nebraska Center for Mass Spectrometry. All allylic alcohols were prepared by reduction of corresponding α,β-unsaturated esters or aldehydes with DIBALH.[1] α,β-unsaturated esters were prepared through Horner-Emmons[1] or Wittig[2] olefination, when α,β-aldehydes were prepared through corresponding aldehydes' self-condensation or condensation with formaldehyde.[3]

Preparation of substrates

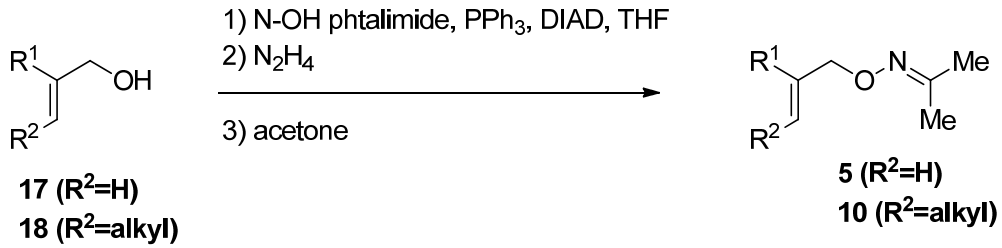


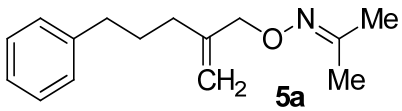


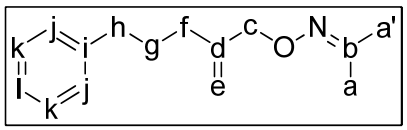


Preparation of unsaturated benzophenone oxime ether 3. Unsaturated benzophenone-derived oxime ether substrate **3** was prepared in two steps from corresponding allylic alcohol **17a**. **Step 1:** To a cooled solution (0 ˚C) of alcohol **17a** (10.0 g, 56.8 mmol) and DMAP (350 mg, 2.86 mmol) in DCM (150 mL) was added pyridine (9.20 mL, 113.7 mmol). Ethyl chloroformate (6.50 mL, 68.2 mmol) was added dropwise over the course of 15 minutes. The reaction mixture was allowed to warm to room temperature overnight. The reaction mixture was washed with water (3 x 25 mL). The organic layer was dried (Na_2SO_4), filtered, and concentrated yielding a yellow oil. Flash chromatography on silica gel (5:95 EtOAc/hexanes) afforded carbonate **18** (13.0 g, 92%) as a

clear oil: TLC analysis (10:90 EtOAc/hexanes) R_f 0.9; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.29 (2H, m, aryl), 7.23-7.20 (3H, m, aryl), 5.13 (1H, s, e), 5.01 (1H, s, e'), 4.61 (2H, s, c), 4.24 (2H, q, *J* = 7.2 *Hz,* b), 2.67 (2H, t, *J* = 7.6 *Hz,* h), 2.16 (2H, t, *J* = 7.8 *Hz,* f), 1.88-1.80 (2H, m, g), 1.35 (3H, t, *J* = 7.0 *Hz,* a); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.19 (m), 143.24 (d), 142.22 (i), 128.55 (j), 128.45 (k), 125.92 (l), 113.11 (e), 70.17 (c), 64.17 (b), 35.55 (f), 32.67 (h), 29.26 (g), 14.41 (a). **Step 2:** $Pd_2(dba)_3$ (137.4 mg, 0.15 mmol) and dppb (153.0mg, 0.36 mmol) were dissolved in THF (15 mL) under N_2 atmosphere and stirred for 5 minutes at RT. Solution of carbonate **18** (1.50 g, 6.00 mmol) in THF (5 mL) was added dropwise and mixture was stirred for 10 minutes. In the same time to a cooled (0 ˚C) solution of benzophenone oxime (1.40 g, 7.10 mmol) in THF (10 mL) was added NaH (158.4 mg, 6.60 mmol) in several portions. The resulting mixture was stirred (10 min) and then transferred to the flask containing carbonate via cannula. The reaction mixture was stirred overnight and afterwards filtered through short plug of silica. The filtrate was concentrated under vacuum and the residue purified via flash chromatography on silica gel (5:95 EtOAc/hexanes) to afford the desired unsaturated benzophenone-derived oxime ether **3** (1.70 g, 79%) as a pale yellow oil: TLC analysis (10:90 EtOAc/hexanes) R_f 0.9; ^{1}H NMR (400 MHz, $CDCl_3$) 7.50-7.47 (2H, m, aryl), 7.42-7.40 (3H, m, aryl), 7.36-7.32 (5H, m, aryl), 7.29-7.25 (2H, m, aryl), 7.20-7.15 (3H, m, aryl), 5.02 (1H, s, e), 4.93 (1H, s, e'), 4.66 (2H, s, c), 2.61 (2H, t, *J* = 7.8 *Hz,* h), 2,11 (2H, t, *J* = 7.6 *Hz*, f), 1.83-1.75 ppm (2H, m, g); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.88 (b), 145.74 (d), 142.51 (aryl), 136.66 (aryl), 133.58 (aryl), 129.35 (aryl), 129.31 (aryl), 128.85 (aryl), 128.59 (aryl), 128.41 (aryl), 128.34 (aryl), 128.17 (aryl), 128.03 (aryl), 125.83 (aryl), 112.11 (e), 77.57 (c), 35.72 (h), 33.11 (f), 29.37 ppm (g); IR (neat) 3025 (C-H aromatic stretching), 2923 (C-H aliphatic stretching), 1742 (C=C stretching), 1602 (C=C stretching), 1494 (C=N stretching), 1027 (C-O stretching), 902 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{25}H_{25}NO$: 378.1834 (M + Na), found: 378.1846 *m/z.*

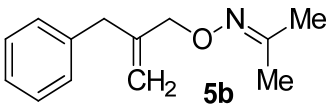


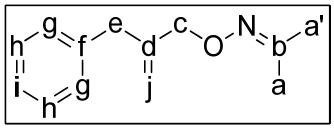




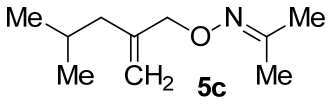
General procedure for the preparation of usaturated acetone oxime ethers (GP1): preparation of 5a. Unsaturated acetone-derived oxime ether substrate **5a** was prepared according to the recently reported procedure by Zhao[4] with minor modification. To a solution (room temperature) of alcohol **17a** (1.0 equiv, 1.00 g, 5.68 mmol), *N*-hydroxyphthalimide (1.1 equiv, 1.02 g, 6.25 mmol) and PPh_3 (1.1 equiv, 1.64 g, 6.25 mmol) in anhyd. THF (11.0 ml) was added diisopropyl azodicarboxylate (1.1 equiv, 1.23 mL, 6.25 mmol) dropwise over 5 minutes. The reaction progress was monitored by TLC (5:95 EtOAc/DCM). After complete consumption of starting materials (typically within 3 h), neat hydrazine (1.2 equiv, 215 µL, 6.82 mmol) was added dropwise. At this point, the formation of milky precipitation was observed. The reaction progress was again monitored by TLC (5:95 EtOAc/DCM). After complete consumption of the first-formed intermediate (typically within 30 minutes), acetone (1.3 equiv, 540 µL, 7.4 mmol) was added. The reaction was again monitored by TLC (1:10 EtOAc/hexanes). After complete reaction (typically 1 h), the resulting mixture was filtered through Celite to

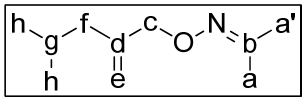
remove precipitate and the filtrate concentrated under reduced pressure. Flash chromatography on silica gel (EtOAc/hexanes 1:20) affords the desired unsaturated acetone-derived oxime ether **5s** (1.15 g, 88 %) as a clear, colorless oil: TLC analysis (10:90 EtOAc/hexanes) R_f 0.9; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.18 (5H, m, aryl), 5.03 (1H, s, e), 4.93 (1H, s, e'), 4.49 (2H, s, c), 2.64 (2H, t, *J* = 7.6 *Hz*, h), 2.14-2.10 (2H, m, f), 1.877 (3H, s, a'), 1.878 (3H, s, a) and 1.87-1.78 ppm (2H, m, g); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.97 (b), 146.09 (d), 142.52 (i), 128.56 (k), 128.38 (j), 125.81 (l), 111.50 (e), 76.17 (c), 35.67 (h), 32.97 (f), 29.34 (g), 21.98 (a'), and 15.75 ppm (a); IR (neat) 3026 (C-H aromatic stretching), 2917 and 2858 (C-H aliphatic stretching), 1651 (C=C stretching), 1453 (C=N stretching), 1028 (C-O stretching), 895 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{15}H_{21}NO$: 254.1521 (M + Na), found: 254.1512 *m/z*.



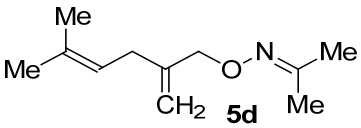


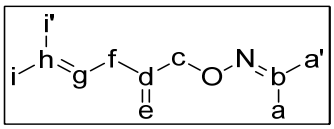
Preparation of unsaturated oxime ether 5b. Using the general procedure (GP1), allylic alcohol **17b** (0.47 g, 3.18 mmol) gave **5b** (0.50 g, 77 %) as a clear, colorless oil: TLC analysis (10:90 EtOAc/hexanes) R_f 0.9; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.18 (5H, m, aryl), 5.11 (1H, s, j), 4.92 (1H, s, j'), 4.45 (2H, s, c), 3.40 (2H, s, e), 1.87 (6H, s, a and a'); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.05 (b), 145.77 (d), 139.27 (f), 129.17 (g), 128.42 (h), 126.22 (i), 113.32 (j), 75.52 (c), 40.24 (e), 21.97 (a`), 15.73 (a); IR (neat) 3025 (C-H aromatic stretching), 2909 (C-H aliphatic stretching), 1650 (C=C stretching), 1485 (C=N stretching), 1072 (C-O stretching), 1007 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{13}H_{17}NO$: 226.1208 (M + Na), found: 226.1201 *m/z*.





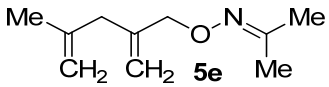
Preparation of unsaturated oxime ether 5c. Using the general procedure (GP1), allylic alcohol **17c** (2.00 g, 17.5 mmol) gave **5c** (2.10 g, 71 %) as a clear, colorless oil: TLC analysis (10:90 EtOAc/hexanes) R_f 0.8; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.03 (1H, s, e), 4.88 (1H, s, e'), 4.46 (2H, s, c), 1.95 (2H, d, *J* = 7.2 *Hz*, f), 1.89 (3H, s, a), 1.88 (3H, s, a'), 1.84-1.75 (1H, m, g), 0.89 ppm (6H, d, *J* = 6.8 *Hz*, h); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.87 (b), 145.26 (d), 112.51 (e), 76.08 (c), 43.40 (f), 26.27 (g), 22.65 (h), 21.99 (a'), and 15.76 ppm (a); IR (neat) 2953, 2920 and 2869 (C-H aliphatic stretching), 1650 (C=C stretching), 1438 (C=N stretching), 1038 (C-O stretching), 896 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{10}H_{19}NO$: 192.1364 (M + Na), found: 192.1358 *m/z*.

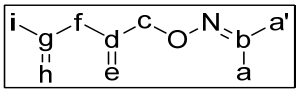




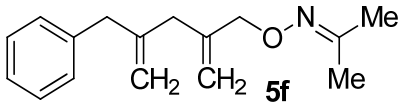
Preparation of unsaturated oxime ether 5d. Using the general procedure (GP1), allylic alcohol **17d** (2.50 g, 19.8 mmol) gave **5d** (2.60 g, 73%) as a clear, colorless oil: TLC analysis (10:90 EtOAc/hexanes) R_f 0.8; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.21 (1H, t, *J* = 7.4 *Hz*, g), 5.00 (1H, s, e), 4.93 (1H, s, e'), 4.49 (2H, s, c), 2.77 (2H, d, *J* = 7.4 *Hz*, f), 1.91 (3H, s, a), 1.90 (3H, s, a'), 1.74 (3H, s, i), 1.64 ppm (3H, s, i'); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.89 (b), 145.76 (d), 133.44 (h), 121.35 (g), 111.23 (e), 76.01 (c), 32.24 (f), 25.85 (i), 21.97 (a'),

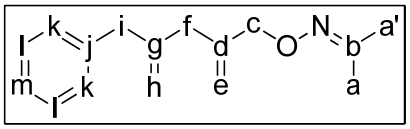
17.72 (i'), 15.73 ppm (a); IR (neat) 2970, 2915 (C-H aliphatic stretching), 1650 (C=C stretching), 1437 (C=N stretching), 1073 (C-O stretching), 896 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{11}H_{19}NO$: 204.1364 (M + Na), found: 204.1360 *m/z*.



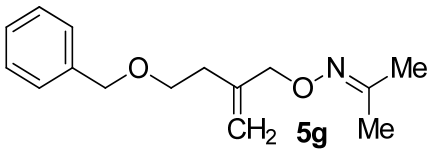


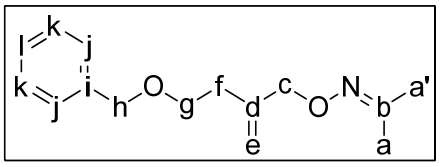
Preparation of unsaturated oxime ether 5e. Using the general procedure (GP1), allylic alcohol **17e** (1.25 g, 11.2 mmol) gave **5e** (1.00 g, 54%) as a clear, colorless oil: TLC analysis (10:90 EtOAc/hexanes) R_f 0.8; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.11 (1H, s, e), 4.98 (1H, s, e'), 4.84 (1H, s, h), 4.79 (1H, s, h'), 4.48 (2H, s, c), 2.81 (2H, s, f), 1.91 (3H, s, a), 1.90 (3H, a'), 1.72 ppm (3H, s, i); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.91 (b), 143.84 (d), 143.05 (g), 113.11 (e), 112.56 (h), 76.37 (c), 42.53 (f), 22.02 (a'), 21.96 (i), 15.73 ppm (a); IR (neat) 3077 (C_{sp2}-H stretching), 2915 (C-H aliphatic stretching), 1644 (C=C stretching), 1435 (C=N stretching), 1076 (C-O stretching), 890 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{10}H_{17}NO$: 190.1208 (M + Na), found: 190.1217 *m/z*.



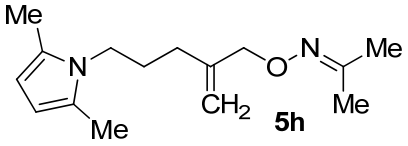


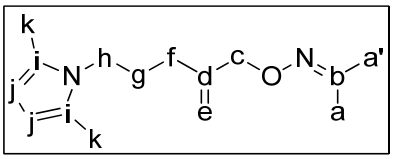
Preparation of unsaturated oxime ether 5f. Using the general procedure (GP1), allylic alcohol **17f** (520 mg, 2.77 mmol) gave **5f** (560 mg, 83 %) as a clear, colorless oil: TLC analysis (10:90 EtOAc/hexanes) R_f 0.8; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33-7.28 (2H, m, aryl), 7.24-7.19 (3H, m, aryl), 5.16 (1H, s, e), 4.98 (1H, s, e'), 4.93 (1H, s, h), 4.86 (1H, s, h'), 4.48 (2H, s, c), 3.35 (2H, s, i), 2.77 (2H, s, f), 1.90 (3H, s, a') 1.89 ppm (3H, s, a); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.98 (b), 146.23 (d), 143.71 (g), 139.73 (j), 129.26 (k), 128.39 (l), 126.19 (m), 113.95 (h), 113.65 (e), 75.39 (c), 42.17 (i), 40.09 (f), 22.00 (a'), 15.76 ppm (a); IR (neat) 3064 (C-H aromatic stretching), 2915 (C-H aliphatic stretching), 1641 (C=C stretching), 1432 (C=N stretching), 1074 (C-O stretching), 896 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{16}H_{21}NO$: 266.1521 (M + Na), found: 266.1530 *m/z*.



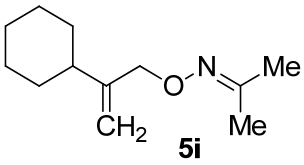


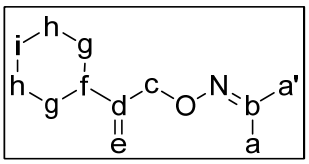
Preparation of unsaturated oxime ether 5g. Using the general procedure (GP1), allylic alcohol **17g** (1.00 g, 5.21 mmol) gave **5g** (1.10 g, 87%) as a clear, colorless oil: TLC analysis (10:90 EtOAc/hexanes) R_f 0.65; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.26 (5H, m, aryl), 5.09 (1H, s, e), 4.99 (1H, s, e'), 4.53 (2H, s, h), 4.51 (2H, s, c), 3.63 (2H, t, *J* = 6.8 *Hz*, g), 2.43 (2H, t, *J* = 6.8 *Hz,* f), 1.872 (3H, s, a'), and 1.868 ppm (3H, s, a); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.98 (b), 143.42 (d), 138.57 (i), 128.48 (k), 127.77 (j), 127.65 (l), 113.14 (e), 76.31 (c), 73.04 (h), 68.91 (g), 33.68 (f), 21.96 (a'), 15.76 ppm (a); IR (neat) 3050 (C-H aromatic stretching), 2916, 2857 (C-H aliphatic stretching), 1651 (C=C stretching), 1453 (C=N stretching), 1076 (C-O stretching), 1027 (C-O stretching), 900 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{15}H_{21}NO_2$: 270.1470 (M + Na), found: 270.1472 *m/z*.



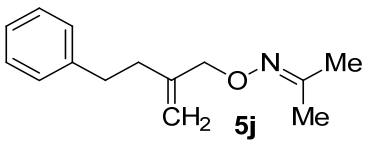


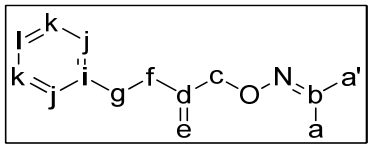
Preparation of unsaturated oxime ether 5h. Using the general procedure (GP1), allylic alcohol **17h** (2.70 g, 14.0 mmol) gave **5h** (2.00 g, 58%) as a clear, colorless oil: TLC analysis (10:90 EtOAc/hexanes) R_f 0.8; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 (2H, s, j), 5.06 (1H, s, e), 4.95 (1H, s, e'), 4.50 (2H, s, c), 3.76-3.72 (2H, m, h), 2.22 (6H, s, k), 2.13 (2H, t, *J* = 7.8 *Hz,* f), 1.88 (6H, s, overlapping a and a'), and 1.85-1.78 ppm (2H, m, g); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.10 (b), 145.34 (d), 127.45 (i), 111.86 (e), 105.20 (j), 76.317 (c), 43.49 (h), 30.50 (f), 28.75 (g), 21.98 (a'), 15.77 (a), 12.62 ppm (k); IR (neat) 3050 (C-H aromatic stretching), 2915 (C-H aliphatic stretching), 1650 (C=C stretching), 1407 (C=N stretching), 1071 (C-O stretching), 1019 (C-N stretching), 896 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{15}H_{24}N_2O$: 271.1786 (M + Na), found: 271.1786 *m/z. [**Note:** We found that compound **5h** is sensitive to air and light and partially decomposes on silica gel.]*



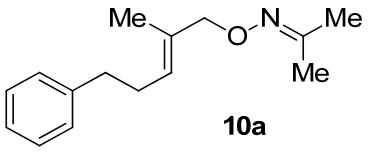


Preparation of unsaturated oxime ether 5i. Using the general procedure (GP1), allylic alcohol **17i** (1.00 g, 7.10 mmol) gave **5i** (1.10 g, 79 %) as a clear, colorless oil: TLC analysis (10:90 EtOAc/hexanes) R_f 0.8; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.01 (1H, s, e), 4.92 (1H, s, e'), 4.55 (2H, s, c), 2.02-1.95 (1H, m, f), 1.91-1.90 (6H, m, a and a'), 1.85-1.69 (5H, m, g, h & i), 1.36-1.15 ppm (5H, m, g', h', i'); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.88 (b), 151.52 (d), 109.55 (e), 75.61 (c), 41.70 (f), 32.40 (g), 26.89 (h), 26.51 (i), 22.02 (a`), 15.88 ppm (a); IR (neat) 2922 and 2851 (C-H aliphatic stretching), 1646 (C=C stretching), 1448 (C=N stretching), 1072 (C-O stretching), 889 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{12}H_{21}NO$: 218.1521 (M + Na), found: 218.1514 *m/z.*

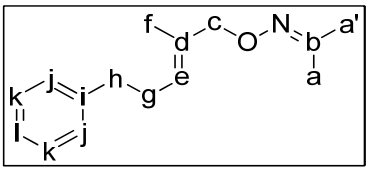




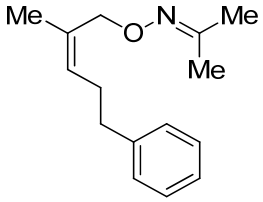
Preparation of unsaturated oxime ether 5j. Using the general procedure (GP1), allylic alcohol **17j** (950 mg, 5.86 mmol) gave **5j** (1.05 g, 83 %) as a clear, colorless oil: TLC analysis (10:90 EtOAc/hexanes) R_f 0.8; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.29 (2H, m, aryl), 7.24-7.19 (3H, m, aryl), 5.07 (1H, s, e), 4.97 (1H, s, e'), 4.56 (2H, s, c), 2.85-2.81 (2H, m, g), 2.44-2.39 (2H, m, f), 1.92 (3H, s, a), 1.92 ppm (3H, s, a'); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.01 (b), 145.84 (d), 142.20 (i), 128.46 (k), 128.42 (j), 125.93 (l), 111.92 (e), 76.27 (c), 35.22 (f), 34.22 (g), 21.99 (a'), 15.79 ppm (a); IR (neat) 3027 (C-H aromatic stretching), 2917 (C-H aliphatic stretching), 1650 (C=C stretching), 1453 (C=N stretching), 1072 (C-O stretching), 897 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{14}H_{19}NO$: 240.1364 (M + Na), found: 240.1369 *m/z.*



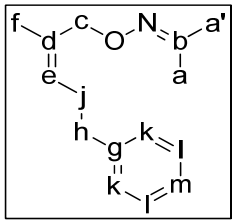
10a



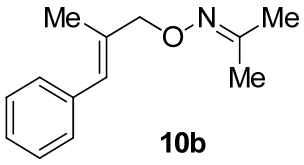
Preparation of unsaturated oxime ether 10a. Using the general procedure (GP1), allylic alcohol **18a** (640 mg, 3.60 mmol) gave **10a** (690 mg, 83%) as a clear, colorless oil: TLC analysis (10:90 EtOAc/hexanes) R_f 0.8; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33-7.28 (2H, m, aryl), 7.23-7.18 (3H, m, aryl), 5.51 (1H, t, , *J* =7.2 Hz, e), 4.44 (2H, s, c), 2.73-2.68 (2H, m, h), 2.43-2.36 (2H, m, g), 1.91 (3H, s, a'), 1.90 (3H, s, a), 1.63 ppm (3H, s, f); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.72 (b), 142.25 (i), 133.02 (d), 128.60 (j), 128.37 (k), 126.93 (e), 125.87 (l), 79.13 (c), 35.82 (h), 29.82 (g), 22.04 (a'), 15.73 (a), 14.03 ppm (f); IR (neat) 3026 (C-H aromatic stretching), 2916 and 2855 (C-H aliphatic stretching), 1603 (C=C stretching), 1453 (C=N stretching), 1015 (C-O stretching), 886 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{15}H_{21}NO$: 254.1521 (M + Na), found: 254.1520 *m/z*.



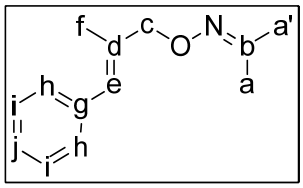
(*Z*)-10a



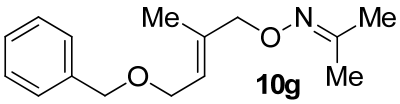
Preparation of unsaturated oxime ether (*Z*)-10a. Using the general procedure (GP1), allylic alcohol **(*Z*)-18a** (500 mg, 2.80 mmol) gave **10a** (510 mg, 79%) as a clear, colorless oil: TLC analysis (10:90 EtOAc/hexanes) R_f 0.8; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.29 (2H, m, aryl), 7.22-7.20 (3H, m, aryl), 5.44 (1H, t, , *J* =7.2 Hz, e), 4.51 (2H, s, c), 2.71-2.67 (2H, m, h), 2.47-2.41 (2H, m, g), 1.90 (3H, s, a'), 1.88 (3H, s, a), 1.79 ppm (3H, s, f); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.81 (b), 142.16 (i), 132.88(d), 128.59 (j), 128.56 (e), 128.40 (k), 125.89 (l), 71.96 (c), 36.34 (h), 29.79 (g), 22.08 (a'), 21.89 (f), 15.67 (a) ppm (f); IR (neat) 3027 (C-H aromatic stretching), 2920 (C-H aliphatic stretching), 1604 (C=C stretching), 1457 (C=N stretching), 1015 (C-O stretching), 890 cm^{-1} (N-O stretching).

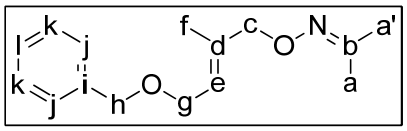


10b

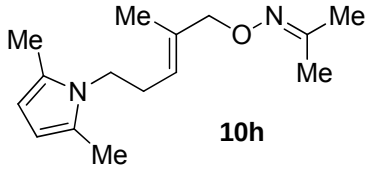


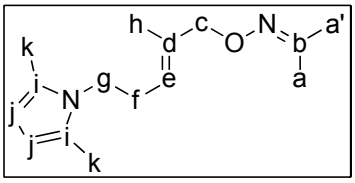
Preparation of unsaturated oxime ether 10b. Using the general procedure (GP1), allylic alcohol **18b** (440 mg, 3.00 mmol) gave **10b** (400 mg, 66%) as a clear, colorless oil: TLC analysis (10:90 EtOAc/hexanes) R_f 0.8; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.29 (4H, m, aryl), 7.26-7.22 (1H, m, aryl), 6.53 (1H, s, e), 4.62 (1H, s, c), 1.96-1.92 ppm (9H, m, f, a & a'); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.09 (b), 137.81 (d), 135.43 (g), 129.11 (p), 128.20 (h), 126.73 (e), 126.51 (j), 79.24 (c), 22.04 (a'), 15.83 (a), 15.62 ppm (f); IR (neat) 3025 (C-H aromatic stretching), 2915 (C-H aliphatic stretching), 1599 (C=C stretching), 1440 (C=N stretching), 1013 (C-O stretching), 884 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{13}H_{17}NO$: 226.1208 (M + Na), found: 226.1214 *m/z*.



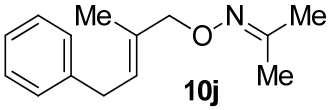


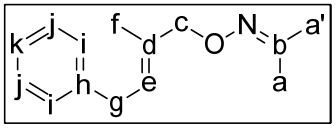
Preparation of unsaturated oxime ether 10g. Using the general procedure (GP1), allylic alcohol **18g** (380 mg, 1.95 mmol) gave **10g** (400 mg, 83%) as a clear, colorless oil: TLC analysis (10:90 EtOAc/hexanes) R_f 0.6; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.28 (5H, m, aryl), 5.69 (1H, qt, *J* =6.8 *Hz, J* =1.4 *Hz*, e), 4.54 (2H, s, h), 4.48 (2H, s, c), 4.12 (2H, d, *J* =6.8 *Hz*, g), 1.91 (3H, s, a), 1.90 (3H, s, a'), 1.70 ppm (3H, s, f); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.95 (b), 138.54 (i), 136.79 (d), 128.48 (k), 127.95 (l), 127.70 (j), 123.29 (e), 78.24 (c), 72.27 (h), 66.34 (g), 21.98 (a'), 15.75 (a), 14.29 ppm (f); IR (neat) 3026 (C-H aromatic stretching), 2916 and 2854 (C-H aliphatic stretching), 1496 (C=C stretching), 1453 (C=N stretching), 1069 (C-O stretching), 1017 (C-O stretching), 883 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{15}H_{21}NO_2$: 270.1470 (M + Na), found: 270.1464 *m/z.*



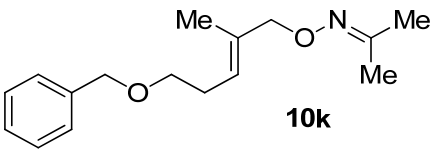


Preparation of unsaturated oxime ether 10h. Using the general procedure (GP1), allylic alcohol **18h** (1.48 g, 7.66 mmol) gave **10h** (1.00 g, 53 %) as a clear, colorless oil: TLC analysis (10:90 EtOAc/hexanes) R_f 0.8; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.76 (2H, s, j), 5.43 (1H, t, *J* = 7.2 *Hz,* e), 4.42 (2H, s, c), 3.77-3.73 (2H, m, g), 2.40-2.34 (2H, m, f), 2.24 (6H, s, k), 1.89 (6H, s, a & a'), 1.62 ppm (3H, s, h); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.91 (b), 135.27 (d), 127.42 (i), 122.67 (e), 105.23 (j), 78.7 (c), 43.14 (g), 29.54 (f), 22.02 (a'), 15.75 (a), 13.89 (h), 12.62 ppm (k); IR (neat) 2915 (C-H aliphatic stretching), 1518 (C=C stretching), 1439 (C=N stretching), 1072 (C-O stretching), 1017 (C-N stretching), 885 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{15}H_{24}N_2O$: 271.1786 (M + Na), found: 271.1777 *m/z. [**Note:** We found compound **10h** is sensitive to air and light and decomposes on silica gel]*

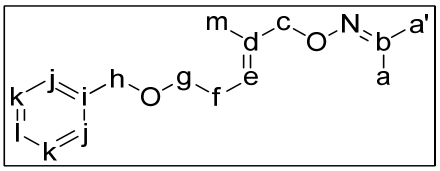




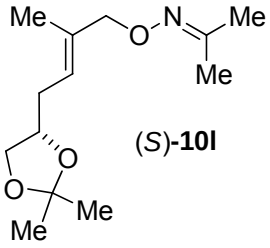
Preparation of unsaturated oxime ether 10j. Using the general procedure (GP1), allylic alcohol **18j** (390 mg, 2.40 mmol) gave **10j** (430 mg, 83%) as a clear, colorless oil: TLC analysis (10:90 EtOAc/hexanes) R_f 0.8; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33-7.29 (2H, m, aryl), 7.23-7.19 (3H, m, aryl), 5.67 (1H, m, e), 4.50 (2H, s, c), 3.46 (2H, d, *J* =7.2 *Hz*, g), 1.91 (6H, s, a and a'), 1.80 ppm (3H, s, f); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.83 (b), 141.12 (d), 133.48 (h), 128.51 (i), 126.27 (j), 125.98 (k), 79.05 (c), 34.02 (g), 22.03 (a'), 15.75 (a), 14.19 ppm (f); IR (neat) 3026 (C-H aromatic stretching), 2915 (C-H aliphatic stretching), 1603 (C=C stretching), 1453 (C=N stretching), 1016 (C-O stretching), 885 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{14}H_{19}NO$: 240.1364 (M + Na), found: 240.1372 *m/z.*



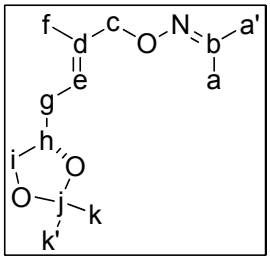
10k



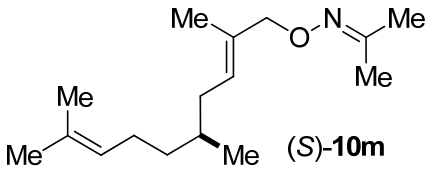
Preparation of unsaturated oxime ether 10k. Using the general procedure (GP1), allylic alcohol **18k** (1.00 g, 4.85 mmol) gave **10k** (1.10 g, 87 %) as a clear, colorless oil: TLC analysis (10:90 EtOAc/hexanes) R_f 0.8; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.26 (5H, m, aryl), 5.47 (1H, t, *J* = 7.0 *Hz,* e), 4.53 (2H, s, h), 4.43 (2H, s, c), 3.50 (2H, t, t, *J* = 7.0 *Hz*, g), 2.40 (2H, q, *J* = 7.0 *Hz,* f), 1.87 (6H, s, a & a'), 1.68 ppm (3H, s, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.76 (b), 138.68 (i), 134.36 (d), 128.49 (k), 127.77 (l or j), 127.65 (l or j), 123.73 (e), 79.08 (c), 73.03 (h), 69.86 (g), 28.59 (f), 22.03 (a'), 15.75 (a), and 14.19 ppm (m); IR (neat) 3025 (C-H aromatic stretching), 2915 (C-H aliphatic stretching), 1601 (C=C stretching), 1453 (C=N stretching), 1072 (C-O stretching), 1016 (C-O stretching), 886 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{16}H_{23}NO_2$: 284.1626 (M + Na), found: 284.1629 *m/z.*



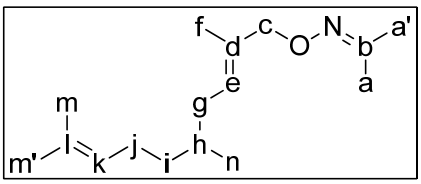
(*S*)-**10l**



Preparation of unsaturated oxime ether (*S*)-10l. Using the general procedure (GP1), allylic alcohol *(S)*-**18l** (1.00 g, 5.40 mmol) gave *(S)*-**10m** (800 mg, 62%) as a clear, colorless oil: TLC analysis (10:90 EtOAc/hexanes) R_f 0.7; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.42 (1H, t, *J* = 7.2 *Hz,* e), 4.41 (2H, s, c), 4.20 (1H, m, h), 4.02 (1H, dd, *J* = 8.0 *Hz,* 6.0 *Hz,* i), 3.56 (1H, tr, m, i'), 2.47-2.40 (1H, m, g), 2.33-2.26 (1H, m, *Hz*, g'), 1.86 (6H, s, a & a'), 1.67 (3H, s, f), 1.42 (k or k'), 1.35 ppm (k or k'); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.82 (b), 135.30 (d), 121.98 (e), 108.99 (j), 78.86 (c), 75.67 (h), 69.14 (i), 32.05 (g), 27.00 (k or k'), 25.81 (k or k'), 21.98 (a'), 15.70 (a), 14.30 ppm (f); IR (neat) 2985 (C-H aliphatic stretching), 2916 (C-H aliphatic stretching), 1438 (C=N stretching), 1062 (C-O stretching), 1017 (C-O stretching), 886 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{13}H_{23}NO_3$: 264.1576 (M + Na), found: 264.2147 *m/z.*

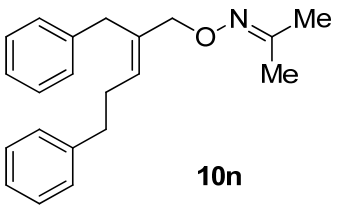


(*S*)-**10m**

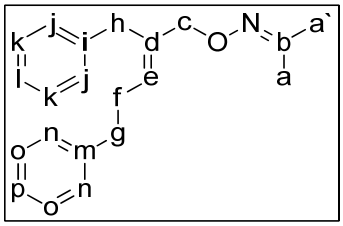


Preparation of unsaturated oxime ether (*S*)-10m. Using the general procedure (GP1), allylic alcohol (*S*)-**18m** (1.30 g, 6.63 mmol) gave (*S*)-**10m** (1.20 g, 72 %) as a clear, colorless oil: TLC analysis (10:90 EtOAc/hexanes) R_f 0.8; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.47 (1H, t, *J* = 7.4 *Hz,* e), 5.12 (1H, t, *J* = 7.2 *Hz,* k), 4.44 (2H, s, c), 2.12-1.91 (4H, m, g & j), 1.91 (3H, s, a or a'), 1.90 (3H, s, a or a'), 1.70 (3H, s, m), 1.68 (3H, s, f), 1.62 (3H, s, m'), 1.58-1.45 (1H, m, h), 1.43-1.32 (1H, m, i), 1.23-1.11 (1H, m, i'), 0.90 ppm (3H, d, *J* = 6.6 *Hz*, n); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.68 (b), 132.8 (d), 131.2 (l), 127.13 (e), 125.07 (k), 79.52 (c), 36.93 (i), 35.05 (g), 33.20 (h), 25.87 (m), 25.82 (j), 22.04 (a'), 19.67 (n), 17.78 (m), 15.74 (a), 14.27 ppm (f); IR (neat) 2913 (C-H

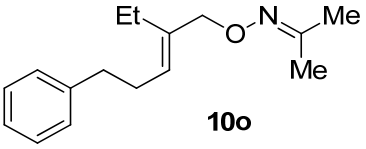
aliphatic stretching), 2853 (C-H aliphatic stretching), 1437 (C=N stretching), 1016 (C-O stretching), 886 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{16}H_{29}NO$: 274.2147 (M + Na), found: 274.2155 *m/z.*



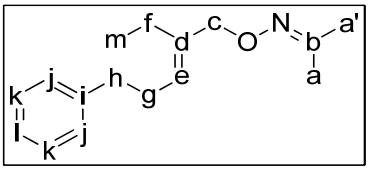
10n



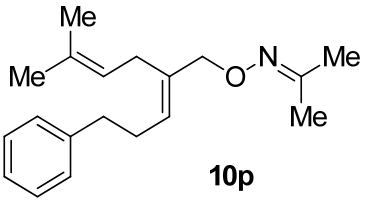
Preparation of unsaturated oxime ether 10n. Using the general procedure (GP1), allylic alcohol **18n** (760 mg, 3.00 mmol) gave **10n** (700 mg, 76%) as a clear, colorless oil: TLC analysis (10:90 EtOAc/hexanes) R_f 0.9; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.13 (10 H, m, aryl), 5.71 (1 H, t, *J* = 7.2 *Hz*, e), 4.41 (2 H, s, c), 3.44 (2 H, s, h), 2.75 (2H, m, g), 2.53 (2H, q, *J* = 7.2 *Hz*, f), 1.87 (3H, s, a'), 1.81 ppm (3H, s, a); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.74 (b), 141.99 (m), 139.81 (i), 135.69 (d), 129.06 (e), 128.69 (aryl), 128.64 (aryl), 128.43 (aryl), 128.38 (aryl), 125.97 (aryl), 125.92 (aryl), 77.20 (c), 35.95 (g), 34.22 (h), 30.14 (f), 21.98 (a'), 15.68 ppm (a); IR (neat) 3025 (C-H aromatic stretching), 2915 (C-H aliphatic stretching), 1601 (C=C stretching), 1452 (C=N stretching), 1071 (C-O stretching), 1006 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{21}H_{25}NO$: 330.1834 (M + Na), found: 330.1848 *m/z.*



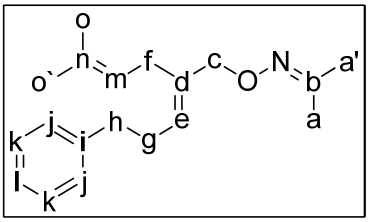
10o



Preparation of unsaturated oxime ether 10o. Using the general procedure (GP1), allylic alcohol **18o** (530 mg, 2.80 mmol) gave **10o** (500 mg, 73%) as a clear, colorless oil: TLC analysis (10:90 EtOAc/hexanes) R_f 0.8; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23-7.18 (2H, m aryl), 7.13-7.08 (3H, m, aryl), 5.40 (1H, t, *J* = 7.2 *Hz,* e), 4.38 (2H, s, c), 2.63-2.58 (2H, m, h), 2.34-2.27 (2H, m, g), 2.00 (2H, q, *J* = 7.6 *Hz,* f), 1.80 (3H, s, a`), 1.79 (3H, s, a), 0.88 ppm (3H, t, *J* =7.6 *Hz,* m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.63 (b), 142.27 (i), 138.61 (d), 128.60 (j), 128.40 (k), 127.17 (e), 125.91 (l), 77.43 (c), 36.16 (h), 29.64 (g), 22.05 (a'), 21.56 (f), 15.82 (a), 13.19 ppm (m); IR (neat) 3027 (C-H aromatic stretching), 2917 and 2856 (C-H aliphatic stretching), 1603 (C=C stretching), 1453 (C=N stretching), 1068 (C-O stretching), 918 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{16}H_{23}NO$: 268.1677 (M + Na), found: 268.1680 *m/z.*

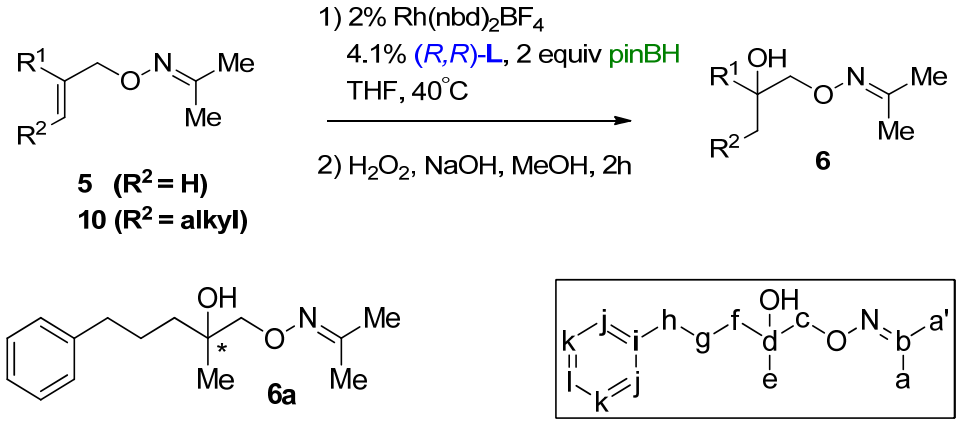


10p

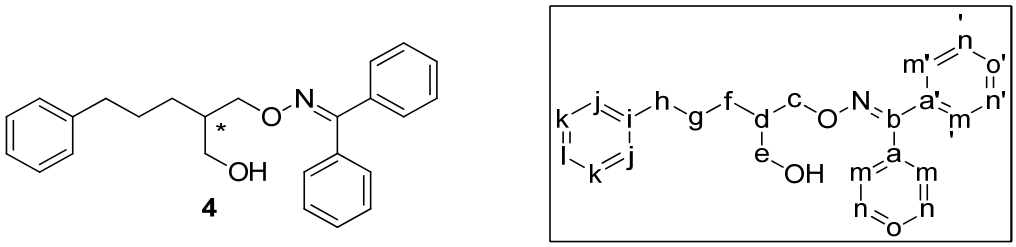


Preparation of unsaturated oxime ether 10p. Using the general procedure (GP1), allylic alcohol **18p** (690 mg, 3.00 mmol) gave **10p** (600 mg, 70%) as a clear, colorless oil: TLC analysis (10:90 EtOAc/hexanes) R_f 0.8; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.28 (2H, m, aryl), 7.23-7.20 (3H, m, aryl), 5.52 (1H, t, *J* =7.2 *Hz,* e), 4.99 (1H, *J* =7.3 *Hz,* m), 4.43 (2H, s, c), 2.78-2.58 (4H, m, f & h), 2.46-2.38 (2H, q, *J* =7.2 *Hz,* g), 1.90 (3H, s, a`),

1.89 (3H, s, a), 1.69 (3H, s, o'), 1.66 ppm (3H, s, o); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.60 (b), 142.23 (i), 136.53 (d), 132.18 (n), 128.63 (j), 128.40 (k), 127.31 (e), 125.91 (l), 122.11 (m), 77.30 (c), 36.10 (h), 29.79 (g), 27.39 (f), 25.88 (o'), 22.05 (a'), 17.87 (o), 15.78 ppm (a); IR (neat) 2914 (C-H aliphatic stretching), 1601 (C=C stretching), 1452 (C=N stretching), 1070 (C-O stretching), 1003 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{19}H_{27}NO$: 308.1990 (M + Na), found: 308.1981 *m/z*.

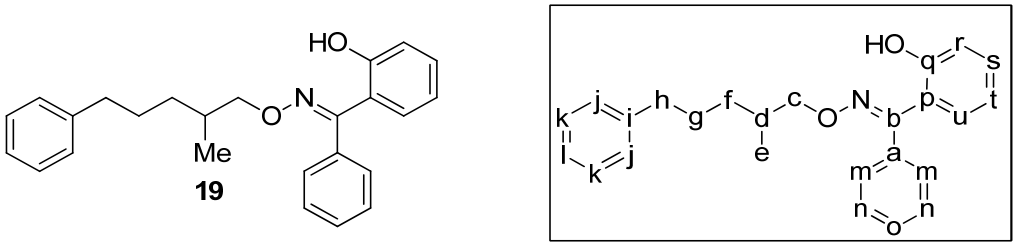


General procedure for CAHB followed by oxidation (GP2) synthesis of 6a. A stock solution of Rhodium-ligand complex was prepared by dissolving $Rh(nbd)_2BF_4$ (2.40 mg, 6.42 μmol) and **(*R,R*)-L** (9.17 mg, 13.1 μmol) in THF (1.2 mL) (room temperature, 1 h). A 1.0 mL aliquot of the resulting yellow solution was added to a solution of unsaturated oxime ether **5a** (61.5 mg, 266 μmol) in THF (4.0 mL). The resulting stirred mixture was warmed (40 ˚C) and solution of pinacolborane (pinBH, 68.1 mg, 532 μmol) in THF (1.0 mL) added dropwise. Reaction mixture was stirred (40 ˚C) for 3 h. Afterwards the reaction mixture was cooled (0 ˚C), diluted with MeOH (3.0 mL) and 3 *M* aq NaOH (4.0 mL) followed by dropwise addition of 30% aq H_2O_2 (0.5 mL). The resulting mixture was warmed to room temperature by removing the ice bath and stirred for additional 2 h. Afterwards the mixture was added to brine (5.0 mL) and extracted with EtOAc (3 x 15 mL). The combined organic layers were dried (anhyd. Na_2SO_4), filtered, and concentrated under reduced pressure. Flash chromatography on silica (progressing from10:90 to 30:70 EtOAc/hexanes) affords the β-hydroxylated product (*R*)-**6a** (47.0 mg, 71%) as a colorless oil: TLC analysis (30:70 EtOAc/hexanes) R_f 0.6; $[\alpha]_D^{210}$ = -10.5˚ (c=1.0, $CHCl_3$); chiral HPLC analysis (Chiralpak IB, 97:3 hexanes/isopropanol@ 1.0 mL/min) showed peaks at 15.46 (*S*-enantiomer, 5.11%) and 16.53 min (*R*-enantiomer, 94.89%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.16 (5H, m, aryl), 3.94 (1H, d, *J* = 11.4 *Hz*, c), 3.91 (1H, d, *J* = 11.4 *Hz*, c') 3.16 (1H, br s, OH), 2.66-2.61 (2H, m, h), 1.87 (3H, s, a'), 1.85 (3H, s, a), 1.78-1.69 (2H, m, g), 1.57-1.51 (2H, m, f), 1.16 ppm (3H, s, e); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.79 (b), 142.56 (i), 128.54 (k), 128.37 (j), 125.80 (l), 79.55 (c), 73.34 (d), 38.93 (f), 36.54 (h), 25.67 (g), 23.77 (a'), 22.01 (e), 15.61 ppm (a); IR (neat) 3427 (O-H stretching), 3026 (C-H aromatic stretching), 2918 (C-H aliphatic stretching), 1603 (C=C stretching), 1375 (C=N stretching), 1071 (C-O stretching), 964 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{15}H_{23}NO_2$: 272.1626 (M + Na), found: 272.1627 *m/z*. In the same reaction conditions unsaturated oxime ether (*E*)-**10a** gave (*S*)-**6a** (55.6 mg, 84% yield): $[\alpha]_D^{210}$ = +12.4˚ (c=1.0, $CHCl_3$); chiral HPLC analysis (Chiralpak IB, 97:3 hexanes/isopropanol@ 1.0 mL/min) showed peaks at 16.06 (*S*-enantiomer, 95.99%) and 17.19 min(*R*-enantiomer, 4.01%). Using the same reaction conditions unsaturated oxime ether (*Z*)-**10a** gave (*S*)-**6a** (36.4 mg, 55% yield): $[\alpha]_D^{210}$ = +10.9˚ (c=1.0, $CHCl_3$); chiral HPLC analysis (Chiralpak IB, 97:3 hexanes/isopropanol@ 1.0 mL/min) showed peaks at 15.53 (*S*-enantiomer, 89.98%) and 17.21 min(*R*-enantiomer, 10.02%).



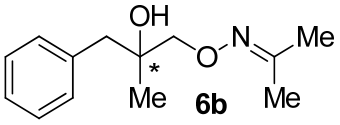
4

Synthesis of 4. Using the general procedure for CAHB (GP2 with the following modifications: *(S,S)*-**L** was used; reaction was stirred at 40 ˚C for 24 h before quenching) unsaturated oxime ether **3** (94.4 mg, 266 μmol) gave alcohol **4** (20.0 mg, 20%) as a clear, colorless oil: TLC analysis (30:70 EtOAc/hexanes) R_f 0.4; chiral HPLC analysis (Chiralpak IC, 95:5 hexanes/isopropanol@ 1.5 mL/min) showed peaks at 29.44 (major enantiomer, 64.58%) and 33.38 min (minor enantiomer, 35.42%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.45 (5H, m, aryl), 7.42-7.25 (7H, m, aryl), 7.22-7.18 (3H, m, aryl), 4.36 (1H, dd, *J* = 10.8 *Hz* & 4.0 *Hz,* c), 4.19 (1H, dd, *J* = 10.8 *Hz* & 7.2 *Hz,* c'), 3.70-3.64 (1H, m, e), 3.61-3.55 (1H, m, e'), 2.65-2.61 (2H, m, h), 2.07-2.04 (1H, m, OH), 2.01-1.93 (1H, m, d), 1.70 (2H, quin, *J* = 7.8 *Hz* ,g), 1.44-1.29 ppm (2H, m, f):^{13}C NMR (100 MHz, $CDCl_3$) δ 157.42 (b), 142.43 (i), 136.15 (a or a'), 133.33 (a or a'), 129.63 (aryl), 129.09 (aryl), 129.00 (aryl), 128.53 (aryl), 128.46 (aryl), 128.45 (aryl), 128.39 (aryl), 127.92 (aryl), 125.88 (aryl), 76.65 (c), 64.70 (e), 40.89 (d), 36.24 (h), 29.08 (g), 27.86 ppm (f); IR (neat) 3392 (O-H stretching), 3024 (C-H aromatic stretching), 2926 (C-H aliphatic stretching), 1602 (C=C stretching), 1444 (C=N stretching), 1028 (C-O stretching), 982 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{25}H_{27}NO_2$: 396.1939 (M + Na), found: 396.1946 *m/z.*

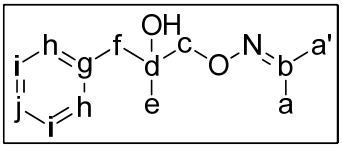


19

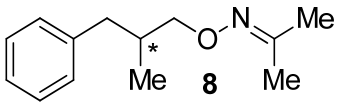
Synthesis of *ortho*-C-H activated benzophenone oxime ether 19. Using the general procedure for CAHB (GP2 with the following modifications: *(S,S)*-**L** was used; reaction was stirred at 40 ˚C for 24 h before quenching; second column (25:75 DCM/Hex) was required to purify C-H activated product **19** from reduced by-product), unsaturated oxime ether **3** (94.4 mg, 266 μmol) gave C-H activation product **19** (60.4 mg, 61%) as a clear, colorless oil: TLC analysis (30:70 EtOAc/hexanes) R_f 0.8; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.22 (1H, s, OH), 7.49-7.46 (3H, m, aryl), 7.28-7.10 (8H, m, aryl), 7.05 (1H, d, *J* = 8.4 *Hz,* aryl), 6.83 (1H, dd, *J* = 8.0 *Hz* & 1.6 *Hz,* aryl), 6.76 (1H, m, aryl), 4.04 (1H, dd, *J* = 10.4 *Hz* & 6.4 *Hz,* c), 3.96 (1H, dd, *J* = 10.4 *Hz* & 6.8 *Hz,* c'), 2.59 (2H, t, *J* = 6.8 *Hz*, h), 1.99-1.91 (1H, m, d), 1.72-1.56 (2H, m, g), 1.45-1.37 (1H, m, f), 1.21-1.12 (1H, m, f'), 0.90 ppm (3H, d, *J* = 6.4 *Hz,* e); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.56 (b), 158.36 (q), 142.60 (i), 132.07 (a), 130.90 (aryl), 130.64 (aryl), 128.98 (aryl), 128.54 (aryl), 128.41 (aryl), 128.38 (aryl), 125.81 (aryl), 118.96 (t), 118.87 (p), 117.23 (r), 80.45 (c), 36.24 (h), 33.08 (f), 32.78 (d), 28.75 (g), 16.86 ppm (e); IR (neat) 3427 (O-H stretching), 3025 (C-H aromatic stretching), 2925 (C-H aliphatic stretching), 1444 (C=N stretching), 1030 (C-O stretching), 1000 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{25}H_{27}NO_2$: 396.1939 (M + Na), found: 396.1929 *m/z.*



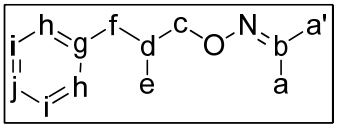
6b



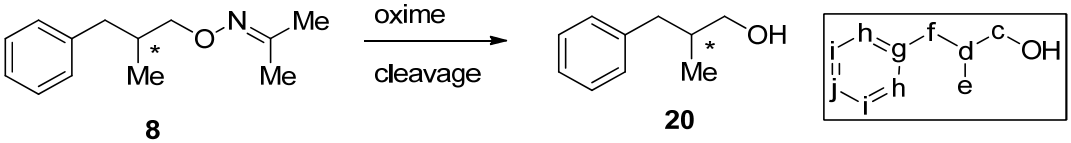
Synthesis of 6b. Using the general procedure for CAHB (GP2) unsaturated oxime ether **5b** (54.2 mg, 0.266 μmol) gave alcohol *(R)*-**6b** (41.0 mg, 70%) as a clear, colorless oil: TLC analysis (30:70 EtOAc/hexanes) R_f 0.6; $[\alpha]_D$ = -29.4˚ (c = 1.00, $CHCl_3$); chiral HPLC analysis (Chiralpac-AD, 90:10 hexanes/isopropanol @ 1.0 mL/min) showed peaks at 11.54 (*R*-enantiomer, 93.83%) and 12.85 min (*S*-enantiomer, 6.17%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.22 (5H, m, aryl), 3.92 (2H, s, c), 3.31 (1H, br s, OH), 2.87 (1H, d, *J* = 13.2 *Hz*, f), 2.81 (1H, d, *J* = 13.2 *Hz*, f'), 1.92 (3 H, s, a or a'), 1.90 (3H, s, a or a'), 1.14 ppm (3H, s, e); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.93 (b), 137.69 (g), 130.68 (h), 128.19 (i), 126.41 (j), 78.65 (c), 73.68 (d), 45.53 (f), 23.85 (e), 22.02 (a'), 15.73 ppm (a); IR (neat) 3435 (O-H stretching), 2920 (C-H aliphatic stretching), 1642 (C=C stretching), 1450 (C=N stretching), 1044 (C-O stretching), 910 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{13}H_{19}NO_2$: 244.1313 (M + Na), found: 244.1304 *m/z*. In the same reaction conditions **10b** (54.2 mg, 0.266 mmol) gave alcohol *(S)*-**6b** (33.5 mg, 57%); chiral HPLC analysis (Chiralpac-AD, 90:10 hexanes/isopropanol @ 1.0 mL/min) showed peaks at 12.1 (*R*-enantiomer, 23.6%) and 14.1 min (*S*-enantiomer, 76.4%).



8



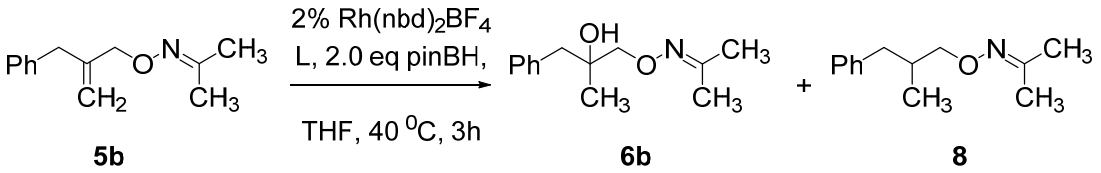
Synthesis of 8. Using the representative procedure for CAHB (GP2), unsaturated oxime ether **5b** (54.0 mg, 266 μmol) gave reduced by-product **8** (11.3 mg, 21%) as a clear, colorless oil: TLC analysis (10:90 EtOAc/hexanes) R_f 0.8; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.28 (2H, m, aryl), 7.23-7.18 (3H, m, aryl), 3.97-3.86 (2H, m, c), 2.83 (1H, dd, *J* =13.5 *Hz* & 5.7 *Hz*, f), 2.42 (1H, dd, *J* =13.5 *Hz* & 8.4 *Hz*, f'), 2.20-2.13 (1H, m, d), 1.91 (3H, s, a'), 1.90 (3H, s, a), 0.93 ppm (3H, d, *J* =6.6 *Hz*, e); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.56 (b), 140.79 (g), 129.38 (h), 128.27 (i), 125.88 (j), 78.03 (c), 40.05 (f), 35.07 (d), 22.00 (a'), 16.68 (e), 15.66 ppm (a); IR (neat) 3026 (C-H aromatic stretching), 2918 and 2856 (C-H aliphatic stretching), 1603 (C=C stretching), 1453 (C=N stretching), 1068 (C-O stretching), 1040 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{13}H_{19}NO$: 228.1364 (M + Na), found: 228.1366 *m/z*.



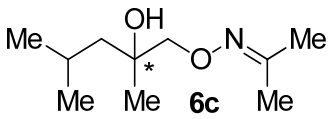
8 **20**

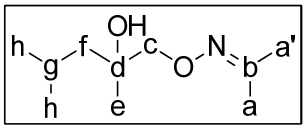
Enantioselectivity of reduced by-product **8** was found after cleavage of oxime and HPLC analysis of 2-methyl-3-phenyl-1-propanol **20**. Using N-O bond cleaving procedure (see synthesis of diol **11**), **8** (20.5 mg, 1mmol) was converted to 2-methyl-3-phenyl-1-propanol **20** with 75% yield (NMR data of product is consistent with lit. [5]): TLC analysis (30:70 EtOAc/hexanes) R_f 0.5; chiral HPLC analysis (Chiralpak-OD, 80:20 hexanes/isopropanol @ 1.0 mL/min) showed peaks at 10.14 (44.6%) and 12.50 min (55.4%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.29 (2H, m, aryl), 7.25-7.19 (3H, m, aryl), 3.60-3.47 (2H, m, c), 2.79 (1H, dd, *J* =13.5 *Hz* & 6.3 *Hz*, f), 2.46 (1H, dd, *J* =13.5 *Hz* & 8.0 *Hz*, f), 2.04-1.92 (1H, m, d), 1.52 (1H, br s, OH), 0.95 ppm (3H, d, *J* =6.9 *Hz*, e); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.75 (g), 129.26 (h), 128.38 (i), 126.00 (j), 67.77 (c), 39.82 (f), 37.91 (d), 16.58 ppm (e).

Table 1. Effect of changing the L:Rh ratio.

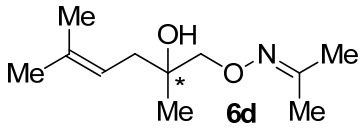


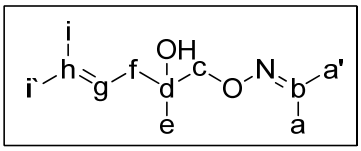
L:Rh	Recovery of **5b**, %	NMR yield of **6b**, %	NMR yield of **8**, %	**6b** : **8** ratio
1.0	0	70	30	2.3 : 1.0
2.0	0	75	25	3.0 : 1.0
3.0	100	0	0	ND



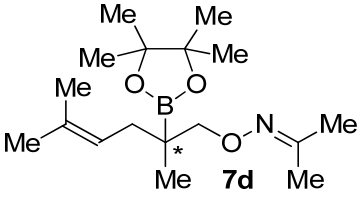


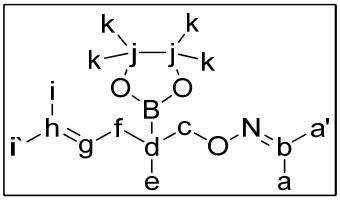
Synthesis of 6c. Using the general procedure for CAHB (GP2) unsaturated oxime ether **5c** (45.1 mg, 266 μmol) gave alcohol *(R)*-**6c** (34.7 mg, 70%) as a clear, colorless oil: TLC analysis (30:70 EtOAc/hexanes) R_f 0.4; $[\alpha]_D$ = -18.2˚ (c = 0.67, $CHCl_3$); chiral GC analysis (Cyclosil β, 90˚ isoterm) showed peaks at 15.7 (*S*-enantiomer, 5.12%) and 16.23 min (*R*-enantiomer, 94.88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.94 (1H, d, *J* = 11.2 *Hz,* c), 3.88 (1H, d, *J* = 11.2 *Hz,* c'), 3.04 (1H, br.s, OH), 1.88 (3H, s, a or a'), 1.87 (3H, s, a or a'), 1.86-1.78 (1H, m, g), 1.40 (2H, d, *J* = 6.0 *Hz,* f), 1.19 (3H, s, e), 0.97 (3H, d, *J* = 6.9 *Hz,* h), 0.95 ppm (3H, d, *J* = 6.9 *Hz,* h'); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.67 (b), 80.19 (c), 73.79 (d), 47.86 (f), 25.00 (h), 24.82 (h'), 24.33 (e), 24.08 (g), 21.99 (a'), and 15.64 ppm (a); IR (neat) 3442 (O-H stretching), 2919 (C-H aliphatic stretching), 1456 (C=N stretching), 1048 (C-O stretching), 1025 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{10}H_{21}NO_2$: 210.1470 (M + Na), found: 210.1463 (M + Na) *m/z.*



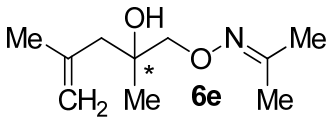


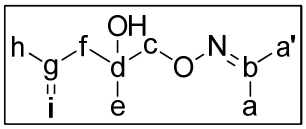
Synthesis of 6d. Using the general procedure for CAHB (GP2 with an exception that unsaturated oxime ether was used crude instead of solution in 4.0 mL of THF), unsaturated oxime ether **5d** (48.2 mg, 266 μmol) gave alcohol (*R*)-**6d** (35.5 mg, 67%) as a clear, colorless oil: TLC analysis (30:70 EtOAc/hexanes) R_f 0.55; $[\alpha]_D$= -19.3˚ (c = 0.5, $CHCl_3$); chiral GC analysis (CP-Chirasil-DEX CB, 95 ˚C isoterm) showed peaks at 41.5 (*S*-enantiomer, 5.46%) and 42.18 min (*R*-enantiomer, 94.54%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.24 (1H, t, *J* = 7.7 *Hz,* g), 3.95 (1H, d, *J* = 11.4 *Hz*, c), 3.90 (1H, d, *J* = 11.4 *Hz*, c'), 2.24 (2H, d, *J* = 7.8 *Hz,* f), 1.902 (3H, s, a) 1.896 (3H, s, a'), 1.75 (3H, s, i'), 1.65 (3H, s, i), 1.17 ppm (3H, s, e); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.67 (b), 134.59 (h), 119.51 (g), 79.20 (c), 73.95 (d), 37.89 (f), 26.16 (i'), 23.83 (e), 22.03 (a'), 18.05 (i), 15.66 ppm (a); IR (neat) 3416 (O-H stretching), 2971 and 2916 (C-H aliphatic stretching), 1643 (C=C stretching), 1375 (C=N stretching), 1071 (C-O stretching), 1045 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{11}H_{21}NO_2$: 222.1470 (M + Na), found: 222.1468 *m/z.*



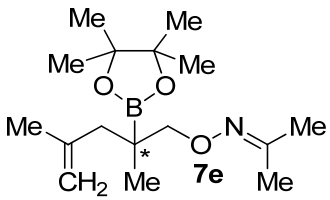


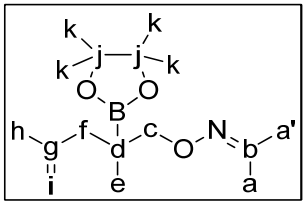
Synthesis of 7d. Using the general procedure for CAHB (GP2 with the following exceptions: unsaturated oxime ether was used crude instead of solution in 4.0 mL of THF; after 3 h reaction was concentrated under reduced pressure without previous quenching and boronic ester was purified using flash chromotography 5:95 EtOAc/hexanes), unsaturated oxime ether **5d** (48.2 mg, 266 μmol) gave boronic ester *(R)*-**7d** (69.0 mg, 84%) as a clear, colorless oil: TLC analysis (10:90 EtOAc/hexanes) R_f 0.5; $[\alpha]_D$= -12.4˚ (c = 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.19 (1H, t, *J* = 7.5 *Hz,* g), 4.04 (1H, d, *J* =9.0 *Hz*, c), 3.86 (1H, d, *J* =9.0 *Hz*, c'), 2.17 (1H, dd, *J* =14.1 *Hz* & 7.5 *Hz*, f), 1.96 (1H, dd, *J* =14.1 *Hz* & 7.8 *Hz,* f'), 1.86 (3H, s, a'), 1.85 (3H, s, a), 1.70 (3H, s, i), 1.61 (3H, s, i), 1.23 (12H, s, k), 1.01 ppm (3H, s, e); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.65 (b), 132.76 (h), 121.65 (g), 83.16 (j), 80.51 (c), 33.95 (f), 26.16 (i'), 24.89 (d), 24.80 (k), 21.95 (a'), 19.26 (i), 18.03 (e), 15.64 ppm (a); ^{11}B NMR (96 MHz, $CDCl_3$) δ 34.92 ppm; IR (neat) 2977 and 2916 (C-H aliphatic stretching), 1458 (C=N stretching), 1357 (B-O stretching), 1144 (C-O stretching), 968 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{17}H_{32}NO_3B$: 332.2373 (M + Na), found: 332.2367 *m/z.*





Synthesis of 6e. Using the general procedure for CAHB (GP2 with the following exceptions: unsaturated oxime ether was used crude instead of solution in 4.0 mL of THF and reaction was stirred at 50 ˚C for 12 h), unsaturated oxime ether **5e** (44.5 mg, 266 μmol) gave alcohol *(R)*-**6e** (24.0 mg, 49%) as a clear, colorless oil: TLC analysis (30:70 EtOAc/hexanes) R_f 0.6; $[\alpha]_D$= -6.7˚ (c = 0.67,$CHCl_3$); chiral GC analysis (Chirasil-DEX CB, 85˚C isoterm) showed peaks at 33.65 (*S*-enantiomer, 3.95 %) and 34.16 min (*R*-enantiomer, 96.05%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.91 (1H, s, h), 4.77 (1H, s, h'), 3.98 (1H, d, *J* = 11.6 *Hz,* c), 3.92 (1H, d, *J* = 11.6 *Hz,* c`), 3.17 (1H, s, OH), 2.26 (2H, s, f), 1.91 (3H, s, a), 1.90 (3H, s, a`), 1.86 (3H, s, h), 1.21 ppm (3H, s, e); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.74 (b), 142.59 (g), 114.80 (i), 79.67 (c), 73.25 (d), 46.95 (f), 24.76 (h), 24.36 (e), 21.99 (a'), 15.66 ppm (a); IR (neat) 3370 (O-H stretching), 2918 (C-H aliphatic stretching), 1601 (C=C stretching), 1457 (C=N stretching), 1047 (C-O stretching), 1024 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{10}H_{19}NO_2$: 208.1313 (M + Na) , found: 208.1314 *m/z.*



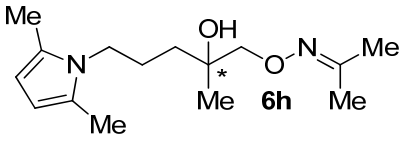


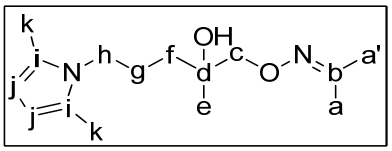
Synthesis of 7e. Using the general procedure for CAHB (GP2 with the following exceptions: unsaturated oxime ether was used crude instead of solution in 4.0 mL of THF; reaction was held at 50 ˚C for 12 h and concentrated under reduced pressure; boronic ester was purified using flash chromotography 5:95 EtOAc/hexanes), unsaturated oxime ether **5e** (44.5 mg, 266 μmol) gave boronic ester *(R)*-**7e** (54.3 mg, 69%) as a clear, colorless

oil: TLC analysis (10:90 EtOAc/hexanes) R_f 0.50; $[\alpha]_D$= -14.6˚ (c = 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.78 (1H, d, *J* = 0.6 *Hz,* i), 4.72 (1H, s, i'), 4.05 (1H, d, *J* = 9.2 *Hz,* c), 3.85 (1H, d, *J* = 9.2 *Hz,* c'), 2.27 (1H, d, *J* = 14.0 *Hz,* f), 2.01 (1H, d, *J* = 14.0 *Hz,* f'), 1.862 (3H, s, a or a`), 1.860 (3H, s , a or a`), 1.75 (3H, s, h), 1.244 (6H, s, k), 1.236 (6H, s, k'), 1.03 ppm (3H, s, e); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.75 (b), 143.87 (g), 112.95 (i), 83.33 (j), 80.95 (c), 43.19 (f), 25.05 (k'), 24.97 (d), 24.91 (k), 24.49 (h), 21.93 (a'), 19.53 (e), 15.67 ppm (a); ^{11}B NMR (96 MHz, $CDCl_3$) δ 34.06 ppm; IR (neat) 2978 and 2918 (C-H aliphatic stretching), 1642 (C=C stretching), 1458 (C=N stretching), 1370 (B-O stretching), 1143 (C-O stretching), 1034 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{16}H_{30}NO_3B$: 318.2216 (M + Na), found: 318.2224 *m/z.*

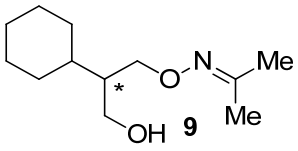
Synthesis of 6f. Using the general procedure for CAHB (GP2 with the following exceptions: unsaturated oxime ether was used crude instead of solution in 4.0 mL of THF and reaction was held at 50 ˚C for 12 h), unsaturated oxime ether **5f** (64.6 mg, 266 μmol) gave alcohol *(R)*-**6f** (36.9 mg, 53%) as a clear, colorless oil: TLC analysis (30:70 EtOAc/hexanes) R_f 0.60; $[\alpha]_D$ = -2.7˚ (c = 1.0, $CHCl_3$); chiral HPLC analysis (Chiralpak-AD, 90:10 hexanes/isopropanol@ 1.0 mL/min) showed peaks at 12.97 (*S*-enantiomer, 4.25%) and 13.77 min (*R*-enantiomer, 95.75%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33-7.28 (2H, m, aryl), 7.24-7.21 (3H, m, aryl), 4.94-4.93 (2H, m, i), 4.00 (1H, d, *J* = 11.2 *Hz,* c), 3.95 (1H, d, *J* = 11.2 *Hz,* c'), 3.53 (2H, s, h), 3.23 (1H, br s, OH), 2.27 (1H, d, *J* = 13.7 *Hz,* f), 2.17 (1H, d, *J* = 13.7 *Hz,* f'), 1.90 (3H, s, a`), 1.88 (3H, s, a), 1.24 ppm (3H, s, e); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.89 (b), 145.77 (g), 140.14 (i), 129.41 (j), 128.36 (k), 126.11 (l), 116.03 (i), 79.76 (c), 73.57 (g), 44.36 (h), 44.02 (f), 24.45 (e), 22.03 (a'), 15.69 ppm(a); IR (neat) 3428 (O-H stretching), 2920 (C-H aliphatic stretching), 1637 (C=C stretching), 1444 (C=N stretching), 1044 (C-O stretching), 909 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{16}H_{23}NO_2$: 284.1626 (M + Na), found: 284.1638 *m/z.*

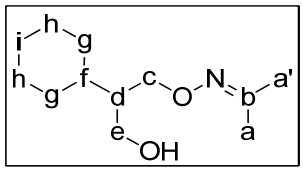
Synthesis of 6g. Using the general procedure for CAHB (GP2 with an exception that reaction was held at 40 ˚C for 6 h), unsaturated oxime ether **5g** (65.8 mg, 266 μmol) gave alcohol *(R)*-**6g** (47.2 mg, 67%) as a clear, colorless oil: TLC analysis (30:70 EtOAc/hexanes) R_f 0.35; $[\alpha]_D$= -3.4˚ (c =1.0, $CHCl_3$); chiral HPLC analysis (Chiralpak-IC, 95:5 hexanes:isopropanol @ 1.0 mL/min) showed peaks at 36.5 (*S*-enantiomer, 4.6%) and 37.7 min (*R*-enantiomer, 95.4%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.27 (5H, m, aryl), 4.52 (2H, s, h), 3.98 (1H, d, *J* = 11.2 *Hz,* c), 3.95 (1H, d, *J* = 11.2 *Hz,* c') , 3.73-3.67 (3H, m, g and OH), 1.93-1.81 (8H, m, a, a' & f), 1.22 ppm (3H, s, e); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.44 (b), 138.22 (i), 128.52 (k), 127.79 (j), 127.77 (l), 79.78 (c), 73.36 (h), 72.63 (d), 67.18 (g), 38.16 (f), 24.75 (e), 21.96 (a'), and 15.67 ppm (a); IR (neat) 3456 (O-H stretching), 2921 (C-H aliphatic stretching), 1717 (C=C stretching), 1366 (C=N stretching), 1072 (C-O stretching), 1026 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{15}H_{23}NO_3$: 288.1576 (M + Na), found: 288.1569 *m/z.* In the same reaction conditions **10g** (65.8 mg, 0.266 mmol) gave mixture of two regioisomeric alcohols and reduced by-product, after flash chromatography alcohol *(S)*-**6g** was obtained (21.0 mg, 30%); chiral HPLC analysis (Chiralpak IC, 95:5 hexanes:isopropanol @ 1.0 mL/min) showed peaks at 34.8 (*S*-enantiomer, 90.3%) and 37.2 min (*R*-enantiomer, 9.7%).



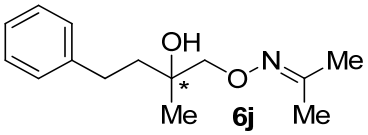


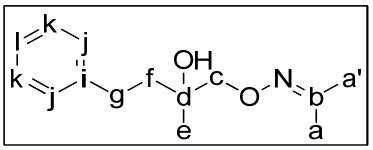
Synthesis of 6h. Using the general procedure for CAHB (GP2 with the following exceptions: solution of catalyst and pinacol borane in 5.0 mL of THF were stirred for 15 min at RT, substrate in 1.0 mL of THF was added; reaction was held at 40 °C for 6 h) unsaturated oxime ether **5h** (66.1 mg, 266 μmol) gave alcohol *(R)*-**6h** (37.5 mg, 53 % [70% from crude NMR with addition of internal standard]) as a clear, yellowish oil: TLC analysis (30:70 EtOAc/hexanes) R_f 0.6; $[\alpha]_D$= -18.5° (c = 1.0, $CHCl_3$); chiral HPLC analysis (Chiralpak-IC, 95:5 hexanes:isopropanol @ 1.0 mL/min) showed peaks at 16.84 (*R*-enantiomer, 94.63%) and 20.58 (*S*-enantiomer, 5.37%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 (2H, s, j), 3.93 (1H, d, *J* = 11.8 *Hz,* c), 3.90 (1H, d, *J* = 11.8 *Hz,* c'), 3.79-3.71 (2H, m, h), 3.24 (1H, br s, OH), 2.24 (6H, s, k), 1.891 (3H, s, a), 1.885(3H, s, a), 1.79-1.68 (2H, m, g), 1.58-1.49 (2H, m, f), 1.16 ppm (3H, s, e); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.94 (b), 127.37 (i), 105. 14 (j), 79.40 (c), 73.10 (d), 44.08 (h) 36.22 (f), 25.47 (g), 23.69 (e), 21.99 (a'), 15.59 (a), 12.62 ppm (k); IR (neat) 3388 (O-H stretching), 2920 (C-H aliphatic stretching), 1716 (C=C stretching), 1368 (C=N stretching), 1111 (C-O stretching), 1070 (C-N stretching), 917 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{15}H_{26}N_2O_2$: 289.1892 (M + Na), found: 289.1878 *m/z.* In the same reaction conditions **10h** also formed alcohol *(S)*-**6h** (39.6 mg, 56 %, [78% from crude NMR with addition of internal standard]); chiral HPLC analysis (Chiralpak-IC, 95:5 hexanes:isopropanol @ 1.0 mL/min) showed peaks at 16.86 (*R*-enantiomer, 5.62%) and 20.58 min (*S*-enantiomer, 94.38%). *[**Note:** We find that compound **6h** is sensitive to air and light and partially decomposes on silica gel.]*



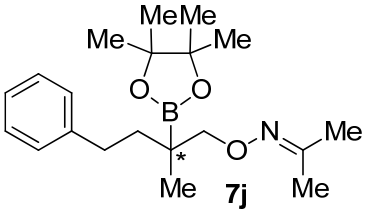


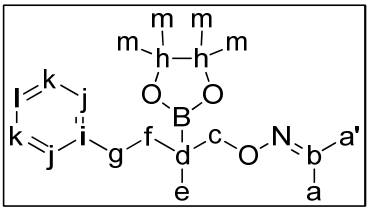
Synthesis of 9. Using the general procedure for CAHB (GP2 with the following exceptions: (*S,S*)-L was used, reaction was held at 40 °C for 24 h), unsaturated oxime ether **5i** (51.9 mg, 266 μmol) gave alcohol **9** (30.5 mg, 54%) as a clear, colorless oil: TLC analysis (30:70 EtOAc/hexanes) R_f 0.45; $[\alpha]_D$= +7.3° (c = 0.7, $CHCl_3$); chiral HPLC analysis of benzyl ester of alcohol (Chiralpak-IC, 95:5 hexanes:isopropanol @ 1.0 mL/min) showed peaks at 16.96 (minor enantiomer, 15.41%) and 17.62 min (major enantiomer, 84.59%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.23 (1H, dd, *J* = 11.0 *Hz* & 4.0 *Hz,* c), 4.15 (1H, dd, *J* = 11.0 *Hz* & 7.2 *Hz,* c'), 3.73-3.72 (2H, m, e), 2.63 (1H, br s, OH), 1.89 (3H, s, a), 1.87 (3H, s, a), 1.79-1.63 (6H, m, g, h, i & d) 1.51-1.43 (1H, m, f), 1.30-1.02 ppm (5H, m, g', h' & i'); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.16 (b), 74.04 (c), 63.16 (e), 46.32 (d), 37.09 (f), 30.86 (g), 30.64 (g'), 26.77 (h), 26.75 (h'), 26.66 (i), 21.98 (a'), 15.75 ppm (a); IR (neat) 3396 (O-H stretching), 2920 and 2850 (C-H aliphatic stretching), 1447 (C=C stretching), 1367 (C=N stretching), 1069 and 1041 (C-O stretching), 922 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{12}H_{23}NO_2$: 236.1626 (M + Na), found: 236.1627 *m/z.*



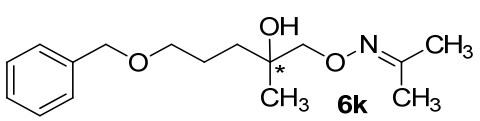


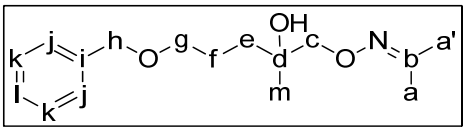
Synthesis of 6j. Using the general procedure for CAHB (GP2), unsaturated oxime ether **5j** (57.8 mg, 0.266 mmol) gave alcohol *(R)*-**6j** (37.4 mg, 60%) as a clear, colorless oil: TLC analysis (30:70 EtOAc/hexanes) R_f 0.6; $[\alpha]_D$= –17.2˚ (c =1.0, $CHCl_3$); chiral HPLC analysis (Chiralpak-IB, 97:3 hexanes:isopropanol @ 1.0 mL/min) showed peaks at 18.6 (*S*-enantiomer, 6.91%) and 21.9 min (*R*-enantiomer, 93.09%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.29 (2H, m, aryl), 7.25-7.19 (3H, m, aryl), 4.04 (1H, d, *J* = 11.6 *Hz,* c), 3.99 (1H, d, *J* = 11.6 *Hz,* c'), 3.31 (1H, br.s, OH), 2.78-2.74 (2H, m, g), 1.92 (6H, s, a & a'), 1.89-1.76 (2H, m, f), 1.27 ppm (3H, s, e); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.91 (b), 142.85 (i), 128.48 (k), 128.45 (j), 125.81 (l), 79.57 (c), 73.28 (d), 41.28 (f), 30.23 (g), 23.84 (e), 22.03 (a'), and 15.67 ppm (a); IR (neat) 3427 (O-H stretching), 2913 and 2860 (C-H aliphatic stretching), 1597 (C=C stretching), 1372 (C=N stretching), 1078 (C-O stretching), 918 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{14}H_{21}NO_2$: 258.1470 (M + Na), found: 258.1470 *m/z.* In the same reaction conditions **10j** formed alcohol *(S)*-**6j** (51.0 mg, 82%) chiral HPLC analysis (Chiralpak IB, 97:3 hexanes:isopropanol @ 1.0 mL/min) showed peaks at 20.91 (*S*-enantiomer, 94.83%) and 25.69 min (*R*-enantiomer, 5.17%).



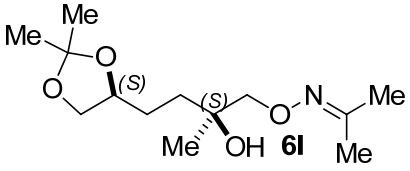


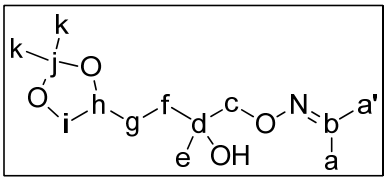
Scale up reaction: synthesis of 7j. General procedure for CAHB (GP2) was used with the following modifications: scale of reaction was increased five-fold, 0.5% catalyst loading, 1.5 eq pinBH, and three-fold increase in reaction mixture concentration were used. A stock solution of rhodium-ligand complex (i.e., Rh[(**L**)$_2$(nbd)]BF_4) was prepared by dissolving Rh(nbd)$_2BF_4$ (2.40 mg, 7.75 μmol) and **(***R,R)*-**L** (11.1 mg, 15.8 μmol) in THF (1.45 mL) (RT, 1 h). A 1.25 mL aliquot of the resulting yellow Rh[(**L**)$_2$(nbd)]BF_4 solution was added to a solution of unsaturated oxime ether **10j** (289 mg, 1.33 mmol) in THF (5.00 mL). The resulting stirred mixture was warmed (40 ˚C) and solution of pinacolborane (pinBH, 255 mg or 0.29 mL, 2.00 mmol) in THF (3.50 mL) added dropwise. The mixture was stirred (40 ˚C) for 7 h. Afterwards, the reaction mixture was concentrated under reduced pressure. Chromatography on silica (5:95 EtOAc/hexanes) affords the β-boronic ester (*S*)-**7j** (350 mg, 78%) as a colorless oil: TLC analysis (10:90 EtOAc/hexanes) R_f 0.8; $[\alpha]_D^{210}$ = +15.5˚ (c=1.0, $CHCl_3$); chiral HPLC analysis of alcohol after oxidative cleavage of boronic ester (Chiralpak-IB, 97:3 hexanes/isopropanol@ 1.0 mL/min) showed peaks at 19.0 (*S*-enantiomer, 93.0%) and 22.6 min (*R*-enantiomer, 7.0%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.27 (2H, m, aryl), 7.23-7.17 (3H, m, aryl), 4.11 (1H, d, *J* = 9.2 *Hz,* c), 3.97 (1H, d, *J* = 9.2 *Hz,* c'), 2.71-2.57 (2H, m, g), 1.89 (3H, s, a'), 1.88 (3H, s, a), 1.87-1.77 (1H, m, f), 1.62-1.55 (1H, m, f'), 1.29 (12H, s, m), 1.12 ppm (3H, s, e); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.85 (b), 143.64 (i), 128.50 (j), 128.37 (k), 125.65 (l), 83.30 (h), 80.50 (c), 38.34 (f), 32.36 (g), 24.96 (m or d), 24.93 (m or d), 21.95 (a'), 19.44 (e), 15.68 ppm (a); IR (neat) 2977 and 2922 (C-H stretching), 1455 (C=N stretching), 1369 and 1312 (B-O stretching), 1143 and 1069 (C-O stretching), 1030 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{20}H_{32}NO_3B$: 368.2373 (M + Na), found: 368.2367 *m/z.*



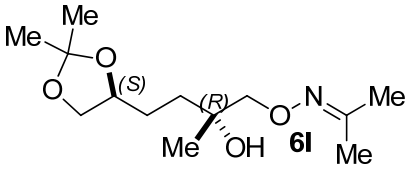


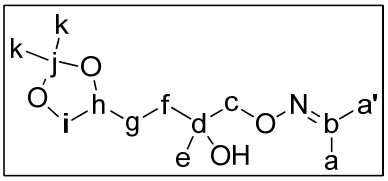
Synthesis of 6k. Using the general procedure for CAHB (GP2 with an exception: reaction was held at 40 ˚C for 6 h), unsaturated oxime ether **10k** (69.5 mg, 266 μmol) gave alcohol *(S)*-**6k** (57.0 mg, 77%) as a clear, colorless oil: TLC analysis (30:70 EtOAc/hexanes) R_f 0.35; $[\alpha]_D$= +2.1˚ (c =1.0, $CHCl_3$); chiral HPLC analysis (Chiralpak-IC, 90:10 hexanes:isopropanol @ 1.0 mL/min) showed peaks at 31.2 (*R*-enantiomer, 6.11%) and 34.6 min (*S*-enantiomer, 93.89%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.25 (5H, m, aryl), 4.51 (2H, s, h), 3.95 (1H, d, *J* = 11.2 *Hz,* c), 3.91 (1H, d, *J* = 11.2 *Hz,* c'), 3.50 (2H, t, *J* = 6.4 *Hz,* g), 3.34 (1H, br. s, OH), 1.87 (6H, s, a & a'), 1.77-1.70 (2H, m, f), 1.65-1.52 (2H, m, e), 1.17 ppm (3H, s, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.66 (b), 138.62 (i), 128.43 (aryl), 127.69 (aryl), 127.58 (aryl), 79.66 (c), 72.95 (d), 72.92 (h), 70.99 (g), 35.95 (e), 24.16 (f), 23.86 (m), 21.96 (a'), and 15.62 ppm (a); IR (neat) 3388 (O-H stretching), 2919 (C-H aliphatic stretching), 1717 (C=C stretching), 1314 (C=N stretching), 1110, 1072 and 1045 (C-O stretching), 1026 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{16}H_{25}NO_3$: 302.1732 (M + Na), found: 302.1728 *m/z.*





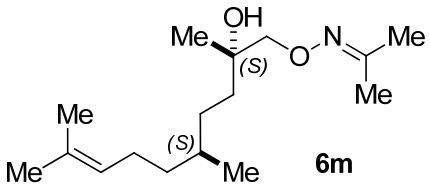
Synthesis of (*S,S*)-6l. Using the general procedure for CAHB (GP2 with an exception: reaction was stirred at 40 ˚C for 6 h), unsaturated oxime ether *(S)*-**10l** (54.5 mg, 266 μmol) gave alcohol (*S,S*)-**6l** (53.0 mg, 77%) as a clear, colorless oil: TLC analysis (30:70 EtOAc/hexanes) R_f 0.35; $[\alpha]_D$= +29.3˚ (c =1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.12-4.03 (2H, m, i, h), 3.95 (1H, d, *J* = 11.6 *Hz,* c), 3.90 (1H, d, *J* = 11.6 *Hz,* c'), 3.56-3.52 (1H, m, i'), 3.33 (0.05 H, minor diastereomer, br s, OH), 3.28 (0.95 H, major diastereomer, br s, OH), 1.89 (3H, s, a), 1.88 (3H, s, a'), 1.78-1.70 (1H, m, g), 1.67-1.62 (2H, m, g' & f), 1.48-1.45 (1H, m, f'), 1.41 (3H, s, k), 1.36 (3H, s, k'), 1.18 ppm (3H, s, e); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.90 (b), 108.93 (j), 79.48 (c), 76.55 (h), 72.96 (d), 69.57 (i), 35.19 (f), 27.95 (g), 27.07 (k'), 25.86 (k), 23.95 (e), 22.04 (a'), 15.69 ppm (a); IR (neat) 3454 (O-H stretching), 2983 and 2934 (C-H aliphatic stretching), 1367 (C=N stretching), 1052 (C-O stretching), 918 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{13}H_{25}NO_4$: 282.1681 (M + Na), found: 282.1674 *m/z.*

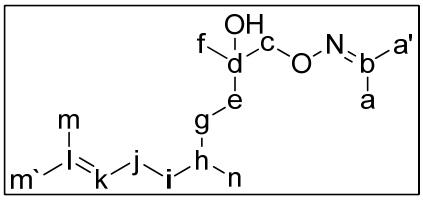




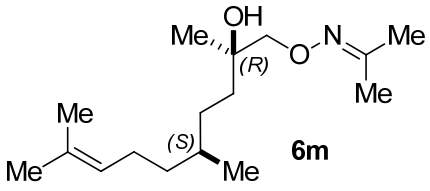
Synthesis of (*R,S*)-6l. Using the general procedure for CAHB (GP2 with the following exceptions: (*S,S*)-**L** was used and reaction was held at 40 ˚C for 6 h), unsaturated oxime ether *(S)*-**10l** (54.5 mg, 0.266 mmol) gave (*R,S*)-**6l** (51.6 mg, 75%) as a clear, colorless oil: TLC analysis (30:70 EtOAc/hexanes) R_f 0.35; $[\alpha]_D$= +1.5˚ (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.12-4.030 (2H, m, i, h), 3.92 (2H, s, c), 3.56-3.52 (1H, m, i'), 3.33 (0.94 H, major diastereomer, br s, OH), 3.29 (0.06 H, minor diastereomer, br s, OH), 1.880 (3H, s, a' or a), 1.876 (3H, s, a' or a), 1.76-1.65 (2H, m, g), 1.61-1.47 (2H, m, f), 1.41 (3H, s, k'), 1.35 (3H, s, k), 1.16 ppm (3H, s, e); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.93 (b), 108.95 (j), 79.55 (c), 76.62 (h), 72.97 (d), 69.60 (i), 35.20 (f),

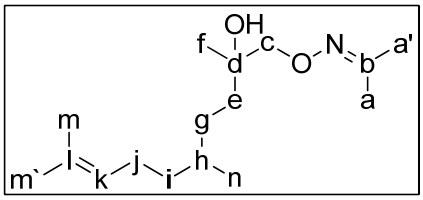
27.92 (g), 27.08 (k'), 25.86 (k), 23.74 (e), 22.04 (a'), 15.68 ppm (a); IR (neat) 3448 (O-H stretching), 2983, 2933 and 2873 (C-H aliphatic stretching), 1369 (C=N stretching), 1052 (C-O stretching), 919 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{13}H_{25}NO_4$: 282.1681 (M + Na), found: 282.1674 *m/z*.





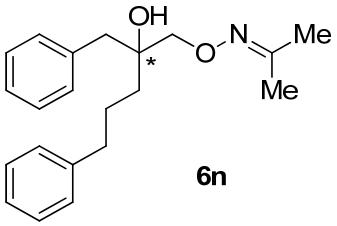
Synthesis of (*S,S*)-6m. Using the general procedure for CAHB (GP2 with the following modification: reaction was held at 40 ˚C for 6 h), unsaturated oxime ether *(S)*-**10m** (64.1 mg, 266 μmol) gave alcohol (*S,S*)-**6m** (57.2 mg, 80%) as a clear, colorless oil: TLC analysis (30:70 EtOAc/hexanes) R_f 0.6; $[\alpha]_D$= +2.3˚ (c = 1.0, $CHCl_3$); ^{1}H NMR (700 MHz, $CDCl_3$) δ 5.11 (1H, t, *J* = 7.0 *Hz,* k), 3.96 (1H, d, *J* = 11.2 *Hz,* c), 3.91 (1H, d, *J* = 11.2 *Hz,* c'), 3.14 (1H, br s, OH), 2.04-1.99 (1H, m, j), 1.97-1.92 (1H, m, j'), 1.894 (3H, s, a), 1.888 (3H, s, a`), 1.69 (3H, s, m'), 1.61 (3H, s, m), 1.55-1.51 (1H, m, e'), 1.48-1.44 (1H, m, e), 1.41-1.33 (3H, m, g, i & h), 1.24-1.20 (1H, m, g'), 1.17-1.15 (4H, m, f & i'), 0.89 ppm (3H, d, *J* = 6.3 *Hz,* n); ^{13}C NMR (175 MHz, $CDCl_3$) δ 155.66 (b), 131.14 (l), 125.07 (k), 79.56 (major diastereomer, 89%, c), 79.51 (minor diastereomer, 11%, c), 73.47 (d), 37.16 (major diastereomer, 91%, i), 37.01 (minor diastereomer, 9%, i), 36.71 (e), 33.02 (h), 30.72 (g), 25.83 (m'), 25.65 (j), 23.80 (minor diastereomer, 10%, f), 23.70 (major diastereomer, 90%, f), 22.011 (a'), 19.72 (minor diastereomer, 9%, n), 19.63 (major diastereomer, 91%, n), 17.74 (m), 15.62 ppm (a); IR (neat) 3430 (O-H stretching), 2917 and 2868 (C-H aliphatic stretching), 1645 (C=C stretching), 1375 (C=N stretching), 1072 and 1043 (C-O stretching), 918 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{16}H_{31}NO_2$: 292.2252 (M + Na), found: 292.2238 *m/z*.



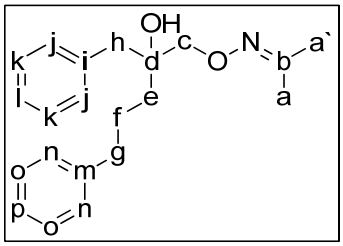


Synthesis of (*R,S*)-6m. Using the general procedure for CAHB (with the following modifications: (*S,S*)-**L** was used; reaction was held at 40 ˚C for 6 h) unsaturated oxime ether *(S)*-**10m** (64.1 mg, 266 μmol) gave alcohol (*R,S*)-**6m** (51.5 mg, 72%) as a clear, colorless oil: TLC analysis (30:70 EtOAc/hexanes) R_f 0.6; $[\alpha]_D$= -0.4˚ (c = 1.0, $CHCl_3$); ^{1}H NMR (700 MHz, $CDCl_3$) δ 5.11 (1H, t, *J* = 7.0 *Hz,* k), 3.96 (1H, d, *J* = 11.2 *Hz,* c), 3.91 (1H, d, *J* = 11.2 *Hz,* c'), 3.14 (1H, br s, OH), 2.04-1.99 (1H, m, j), 1.97-1.93 (1H, m, j'), 1.897 (3H, s, a), 1.892 (3H, s, a'), 1.69 (3H, s, m'), 1.61 (3H, s, m), 1.56-1.51 (1H, m, e), 1.48-1.43 (1H, m, e), 1.41-1.33 (3H, m, g, i & h), 1.21-1.17 (1H, m, g'), 1.17-1.15 (4H, m, f & i'), 0.90 ppm (3H, d, *J* = 6.3 *Hz,* n); ^{13}C NMR (175 MHz, $CDCl_3$) δ 155.69 (b), 131.15 (l), 125.09 (k), 79.57 (minor diastereomer, 11%, c), 79.53 (major diastereomer, 89%, c), 73.47 (d), 37.17 (minor diastereomer, 9%, i), 37.03 (major diastereomer, 91%, i), 36.73 (e), 33.04 (h), 30.73 (g), 25.85 (m'), 25.64 (j), 23.81 (major diastereomer, 91%, f), 23.72 (minor diastereomer, 9%, f), 22.02 (a'), 19.73 (major diastereomer, 91%, n), 19.64 (minor diastereomer, 9%, n), 17.76 (m), 15.64 ppm (a); IR (neat) 3436 (O-H stretching), 2918 and 2869 (C-H aliphatic stretching), 1376 (C=N stretching), 1072 and 1043 (C-O

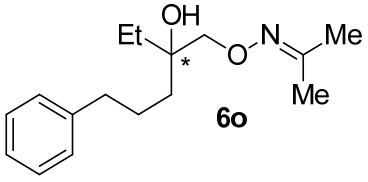
stretching), 919 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{16}H_{31}NO_2$: 292.2252 (M + Na), found: 292.2238 *m/z.*



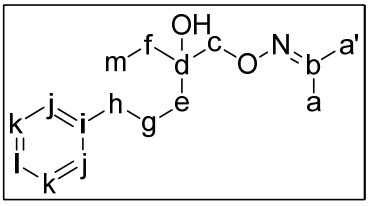
6n



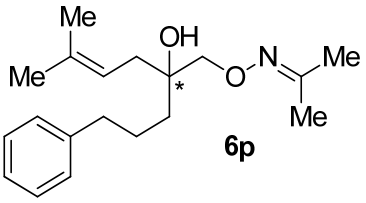
Synthesis of 6n. Using the general procedure for CAHB (GP2 with the following exceptions: unsaturated oxime ether was used crude instead of solution in 4.0 mL of THF and reaction was held at 50 ˚C for 16 h), unsaturated oxime ether **10n** (81.8 mg, 266 μmol) gave alcohol *(S)*-**6n** (60.2 mg, 70%) as a clear, colorless oil: TLC analysis (30:70 EtOAc/hexanes) R_f 0.55; $[\alpha]_D$= -21.0˚ (c = 2.0, $CHCl_3$); chiral HPLC analysis (Chiralpak-OD 97:3 hexanes:isopropanol @ 1.0 mL/min) showed peaks at 23.55 (*S*-enantiomer, 94.1%) and 28.95 min (*R*-enantiomer, 5.9%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.20 (10 H, m, aryl), 3.95 (1H, d, *J* = 11.6 *Hz*, c), 3.89 (1H, d, *J* = 11.6 *Hz*, c'), 3.16 (1H, br s, OH), 2.86 (1H, d, *J* = 13.6 *Hz,* h), 2.82 (1H, d, *J* = 13.6 *Hz,* h'), 2.63 (2H, t, *J* = 7.6 *Hz*, g), 1.90-1.75 (8H, m, a, a' & f) 1.51 ppm (2H, m, e); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.86 (b), 142.56 (m), 137.47 (i), 130.62 (aryl), 128.58 (aryl), 128.38 (aryl), 128.22 (aryl), 126.39 (aryl), 125.81 (aryl), 75.23 (c), 43.26 (h), 36.49 (g), 36.30 (e), 25.37 (f), 22.00 (a'), 15.72 ppm (a); IR (neat) 3446 (O-H stretching), 3026 (C-H aromatic), 2926 and 2856 (C-H aliphatic stretching), 1596 (C=C stretching), 1444 (C=N stretching), 1071 (C-O stretching), 929 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{21}H_{27}NO_2$: 348.1939 (M + Na), found: 348.1940 *m/z.*

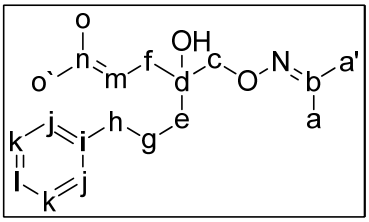


6o

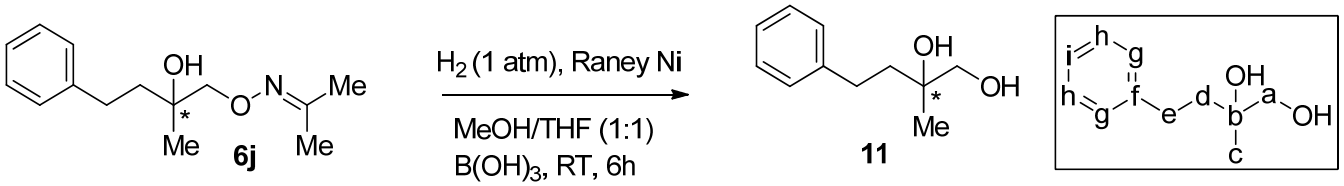


Synthesis of 6o. Using the general procedure for CAHB (GP2 with the following exceptions: unsaturated oxime ether was used crude instead of solution in 4.0 mL of THF and reaction was held at 50 ˚C for 16 h), unsaturated oxime ether **10o** (65.2 mg, 266 μmol) gave alcohol *(S)*-**6o** (51.0 mg, 73%) as a clear, colorless oil: TLC analysis (30:70 EtOAc/hexanes) R_f 0.65; $[\alpha]_D$= +3.8˚ (c = 1.0, $CHCl_3$); chiral HPLC analysis (Chiralpak-AD, 90:10 hexanes:isopropanol @ 1.0 mL/min) showed peaks 11.25 (*S*-enantiomer 82.2%) and 12.01 min (*R*-enantiomer 17.8%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.27 (2H, m, aryl), 7.22-2.17 (3H, m, aryl), 3.97 (2H, s, c), 3.05 (1H, br s, OH), 2.67-2.62 (2H, m, h), 1.89 (3H, s, a or a'), 1.86 (3H, s, a or a'), 1.76-1.66 (2H, m, g), 1.58-1.50 (2H, m, f & e), 0.89 ppm (3H, t, *J* = 7.6 *Hz*, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.72 (b), 142.57 (i), 128.53 (j), 128.36 (k), 125.79 (l), 77.87 (c), 75.17 (d), 36.58 (h), 35.68 (e), 29.13 (f), 25.32 (g), 22.00 (a'), 15.62 (a), 7.93 ppm (m); IR (neat) 3445 (O-H stretching), 3025 (C-H aromatic stretching), 2940 (C-H aliphatic stretching), 1603 (C=C stretching), 1367 (C=N stretching), 1072 and 1042 (C-O stretching), 919 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{16}H_{25}NO_2$: 286.1783 (M + Na), found: 286.1789 *m/z.*



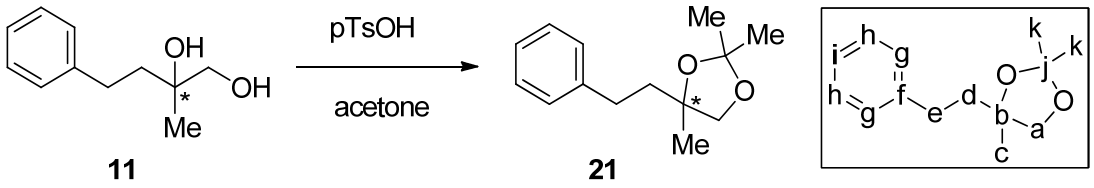


Synthesis of 6p. Using the general procedure for CAHB (GP2 with the following exceptions: unsaturated oxime ether was used crude instead of solution in 4.0 mL of THF and reaction was held at 50 ˚C for 16 h), unsaturated oxime ether **10p** (75.8 mg, 0.266 mmol) gave alcohol *(S)*-**6p** (52.3 mg, 65%) as a clear, colorless oil: TLC analysis (30:70 EtOAc/hexanes) R_f 0.65; $[\alpha]_D$= -11.0˚ (c = 1.0, $CHCl_3$); chiral HPLC analysis (Chiralpak-IB, 97:3 hexanes:isopropanol @ 1.0 mL/min) showed peaks 12.6 (*S*-enantiomer, 85.9%) and 14.2 min (*R*-enantiomer, 14.1%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.27 (2H, m, aryl), 7.22-7.19 (3H, m, aryl), 5.20-5.15 (1H, m, m), 3.94 (2H, s, c), 3.07 (1H, br s, OH), 2.64 (2H, t, *J* = 7.7 *Hz,* h), 2.23 (2H, d, *J* = 7.5 *Hz,* f), 1.89 (a'), 1, 87 (a), 1.80-1.70 (5H, m, o' & g), 1.64 (3H, s, o), 1.56-151 ppm (2H, m, e); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.67 (b), 142.64 (i), 134.55 (n), 128.56 (j), 128.35 (k), 125.78 (l), 119.22 (m), 77.91 (c), 75.47 (d), 36.58 (h), 36.41 (e), 25.50 (f), 26.18 (o'), 25.23 (g), 22.01 (a'), 18.08 (o), 15.67 ppm (a); IR (neat) 3456 (O-H stretching), 3026 (C-H aromatic stretching), 2915 (C-H aliphatic stretching), 1603 (C=C stretching), 1368 (C=N stretching), 1073 and 1042 (C-O stretching), 935 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{19}H_{29}NO_2$: 326.2096 (M + Na), found: 326.2111 *m/z.*

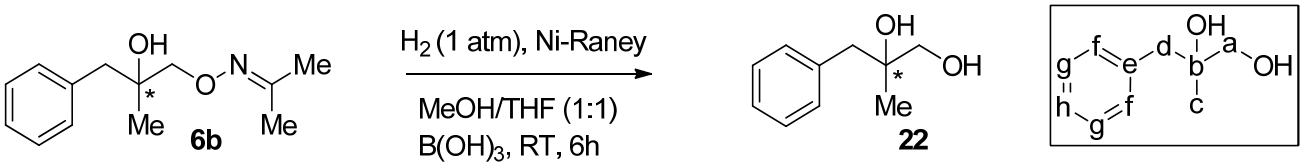


Cleavage of N-O bond (GP3): synthesis of 4-phenyl-2-methyl-1,2-butandiol (11) and absolute configuration determination. Diol **11** was prepared following literature N-O bond cleaving procedure[4] with slight modification. Compound **6j** (50.0 mg, 210 μmol) obtained after CAHB of **10j** using Rh[*(S,S)*-L]$_2$(nbd)BF_4 as a catalyst was dissolved in THF (3.0 mL) and MeOH (3.0 mL). A solution of $B(OH)_3$ (53.8 mg, 870 μmol) in water (1.0 mL) was added to the stirring mixture along with Raney Ni(~ 1.0 mL, 50% in water). The system was purged and stirred rapidly under H_2 (1 atm) for 6 h. The mixture was diluted with 5.0 mL of brine and extracted with EtOAc (3 x 25 mL). The combined organic extracts were washed with 2M HCl (20 mL), dried (anhyd Na_2SO_4), filtered, and concentrated under reduced pressure. Flash chromatography on silica (progressing from 30:70 to 50:50 EtOAc/hexanes) affords diol **11** (30.0 mg, 80 %) (NMR results are consistent with lit. data[6]): TLC analysis (50:50 EtOAc/hexanes) R_f 0.4; $[\alpha]_D$ = -0.34˚ (c = 1.5, EtOH) (reported data[6] $[\alpha]_D$ = -0.52˚ for S-enantiomer with ee=82%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33-7.28 (2H, m, aryl), 7.24-7.19 (3H, m, aryl), 3.54 (1H, d, *J* = 11.0 *Hz*, a), 3.47 (1H, d, *J* = 11.0 *Hz*, a'), 2.75-2.70 (2H, m, e), 2.54 (2H, br s, 2 OH), 1.92-1.81 (2H, m, d), 1.27 ppm (3H, s, c); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.34 (f), 128.54 (g), 128.39 (h), 125.95 (i), 73.03 (a), 69.86 (b), 40.53 (d), 30.17 (e), 23.30 (c) ppm.

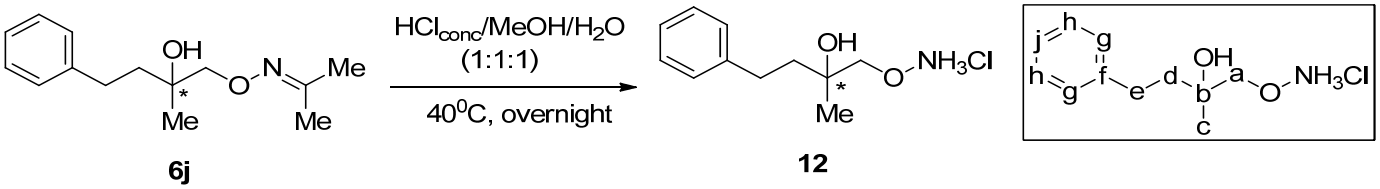
*[**Note:** Specific optical rotation of diol **11** is too small to be reliable for absolute configuration determination, that's why acetonide **21** was prepared and GC traces were compared with literature data in order to assign absolute configuration.[6]]*



Synthesis of acetonide 21. Acetonide **21** was obtained by stirring of diol **11** (15.0 mg, 83 μmol) in acetone (0.40 mL) with catalytic amount of pTsOH overnight. Concentration under reduced pressure with next flash chromatography afforded desired product (11.0 mg, 59% yield): TLC analysis (10:90 EtOAc/hexanes) R_f 0.8; chiral GC analysis of its acetonide (CP-Chirasil-DEX CB, 130^0 isoterm[6]) showed peaks at 28.94 (*S*-enantiomer, 4.23%) and 29.37 min (*R*-enantiomer, 95.77%); ^{1}H NMR (300 MHz, $CDCl_3$) 7.33-7.28 (3H, m, aryl), 7.23-7.18 (2H, m, aryl), 3.87 (1H, d, *J* = 8.4 *Hz*, a), 3.77 (1H, d, *J* = 8.4 *Hz*, a'), 2.82-2.63 (2H, m, e), 1.99-1.81 (2H, m, d), 1.45 (6H, s, k), 1.38 ppm (3H, s, c); ^{13}C NMR (75 MHz, $CDCl_3$) 142.38 (f), 128.57 (g), 128.41 (h), 125.97 (i), 109.37 (j), 81.07 (b), 74.22 (a), 42.13 (d), 30.91 (e), 27.30 (k), 25.00 ppm (c). Based on chiral GC data absolute configuration was assigned: CAHB of **10j** using *(S,S)*-**L** affords (*R)*-**6j.** In order to confirm absolute configuration assignment 3-phenyl-2-methyl-1,2-propandiol (**22**) was prepared.



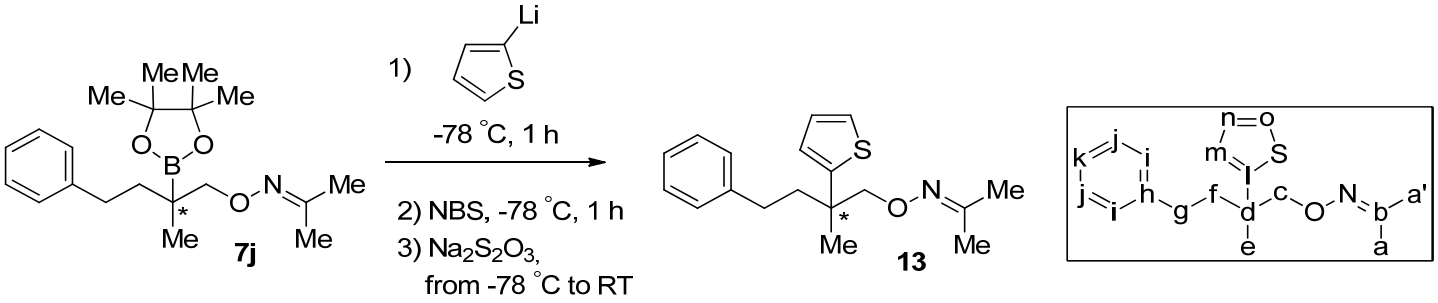
Cleavage of N-O bond: synthesis of 3-phenyl-2-methyl-1,2-propandiol (22) and absolute configuration conformation. Following procedure for N-O bond cleavage (GP3) **6b** (41.0 mg, 190 μmol) obtained after CAHB of **5c** using *(R,R)*-**L** was transformed to diol **22** (30 mg, 97 %) (NMR results are consistent with lit. data[7]): TLC analysis (50:50 EtOAc/hexanes) R_f 0.4; $[\alpha]_D$ = +11.4˚ (c = 1.0, EtOH 95%) (reported data[7] $[\alpha]_D$ = +17.3˚ (c=1.2, EtOH 95%) for R-enantiomer with ee=95%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37-7.24 (5H, m, aryl), 3.51 (1H, d, *J* = 10.8 *Hz*, a), 3.45 (1H, d, *J* = 10.8 *Hz*, a'), 2.88 (1H, d, *J* = 13.2 *Hz*, d), 2.80 (1H, d, *J* = 13.2 *Hz*, d'), 2.20 (1H, br s, OH), 2.04 (1H, br s, OH), 1.16 ppm (3H, s, c); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.09 (e), 130.56 (f), 128.45 (g), 126.75 (h), 73.08 (a), 69.39 (b), 44.76 (d), 23.72 ppm (c). Based on specific optical rotation previous absolute configuration assignment was confirmed: CAHB of **5c** using *(R,R)*-L affords (*R)*-**6c.**



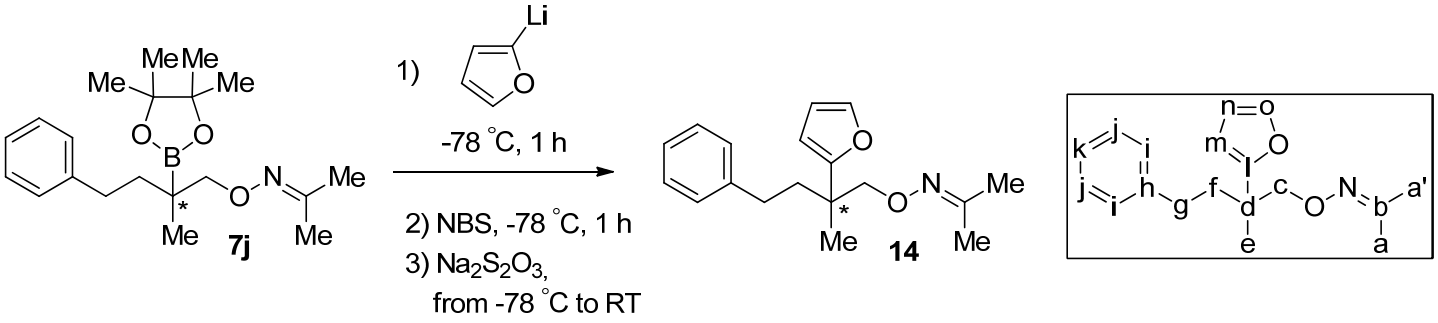
Cleavage of C=N bond: synthesis of 1-(aminooxy)-2-methyl-4-phenylbutan-2-ol hydrochloride 12. Compound **6j** (40.0 mg, 17 μmol) obtained after CAHB of **10j** using *(R,R)*-L was dissolved in a mixture of MeOH (0.3 mL), H_2O (0.3 mL) and HCl_{conc} (0.3 mL) and was stirred in open flask at 40 ^{0}C overnight. Solvents were removed under reduced pressure and compound **12** was obtained as a brown oil (38.5 mg, 98%) and was characterized by NMR without further purification: $[\alpha]_D$ = +8.5˚ (c =1.0, MeOH); ^{1}H NMR (300 MHz, CD_3OD) δ 7.29-7.14 (5H, m, aryl), 4.92 (4H, br s, OH and NH_3^+), 4.01 (1H, d, *J* = 7.8 *Hz,* a), 3.95 (1H, d, *J* = 7.8 *Hz,* a'), 2.74-2.68 (2H, m, e), 1.89-1.82 (2H, m, d), 1.33 ppm (3H, s, c); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.42 (f),

129.40 (g), 129.26 (h), 126.82 (i), 81.49 (a), 73.57 (b), 42.06 (d), 30.77 (e), 23.82 ppm (c); IR (neat) 3319 (O-H stretching), 2936 (C-H stretching), 2684 (N-H stretching), 1602 (C=C stretching), 1454 (C=N stretching), 1023 (C-O stretching), 922 min (N-O stretching). HRMS (ESI) calcd. for free base $C_{11}H_{17}NO_2$: 218.1154 (M + Na), found: 218.1154 *m/z.*

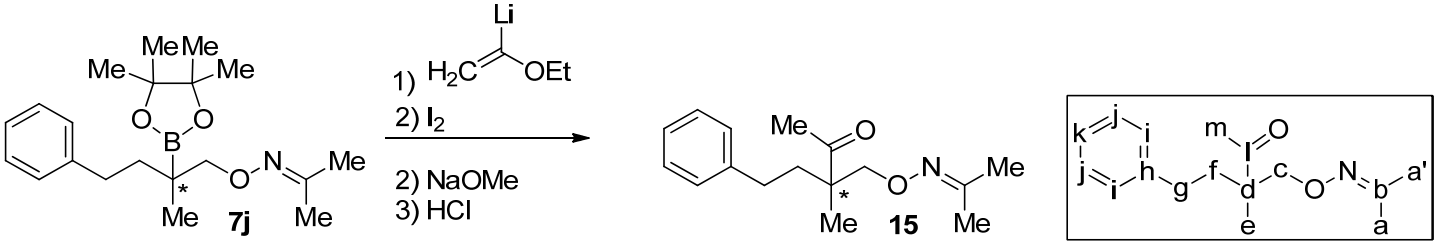
*[**Note:** Before measuring optical rotation and recording IR spectra sample was refluxed with activated carbon in methanol. After filtration and concentration of filtrate under reduced pressure **12** was obtained as a colorless oil (35.0 mg, 91%). NMR results didn't change after this purification step.]*



Enantiospecific sp2–sp3 coupling: synthesis of 13. Following procedure developed by Aggarwal[8] (supporting information, page S-21) a solution of thiophene (36 µL, 450 µmol, 1.3 eq.) in THF (1.5 mL) was cooled (–78 ˚C) and treated with *n*-BuLi (0.2 mL, 450 µmol, 1.3 eq., 2.25 M in hexanes). The cooling bath was removed and the mixture was stirred at room temperature (30 min). Afterwards mixture was cooled (–78 ˚C) and (*S*)-**7j** (118 mg, 342 µmol) was added dropwise as a solution in THF (0.8 mL). The mixture was stirred (–78 ˚C, 1 h) and then a solution of NBS (80.3 mg, 450 µmol, 1.3 eq.) in THF (1.5 mL) was added dropwise. After 1 h at –78 ˚C, $Na_2S_2O_3$ sat (1.5 mL) was added and the reaction mixture was allowed to warm to room temperature. The reaction mixture was diluted with Et_2O (15 mL) and brine (10 mL). The layers were separated and the aqueous layer was extracted with Et_2O (3 x 15 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under vacuum. The crude material was purified by flash chromatography on silica gel (5:95 EtOAc/hexanes) to give (*S*)-**13** (67.6 mg, 65%) as a colorless oil: TLC analysis (50:50 DCM/hexanes) R_f 0.5; $[\alpha]_D$ = -5.1^0 (c = 1.5, $CHCl_3$); chiral HPLC analysis (Chiralpak-AD, 97:3 hexanes:isopropanol @ 1.0 mL/min) showed peaks at 7.58 (*S*-enantiomer, 92.9%) and 8.28 min (*R*-enantiomer, 7.1%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31-7.16 (6H, m, aryl), 7.01-6.98 (1H, m, n), 6.95 (1H, dd, *J* = 3.6 & 1.2 *Hz,* m), 4.22 (1H, d, *J* = 9.8 *Hz,* c), 4.18 (1H, d, *J* = 9.8 *Hz,* c'), 2.64-2.46 (2H, m, g), 2.15-2.01 (2H, m, f), 1.894 (3H, s, a'), 1.889 (3H, s, a), 1.52 ppm (3H, s, e); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.74 (b), 151.24 (l), 142.85 (h), 128.41 (aryl), 126.40 (aryl), 125.75 (aryl), 123.35 (aryl), 123.30 (aryl), 81.65 (c), 42.83 (f), 42.08 (d), 30.77 (g), 24.44 (e), 21.82 (a'), 15.90 ppm (a); IR (neat) 3025 (C-H aromatic stretching), 2917 and 2863 (C-H aliphatic stretching), 1602 (C=C stretching), 1454 (C=N stretching), 1071 (C-O stretching), 997 min (N-O stretching); HRMS (ESI) calcd. for $C_{18}H_{23}NOS$ (M + Na): 324.1390, found: 324.1390 *m/z.*



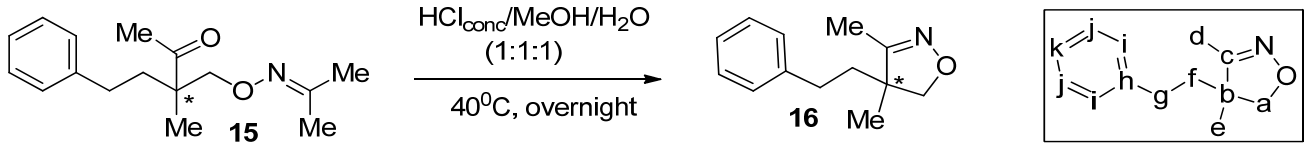
Enantiospecific sp2–sp3 coupling: synthesis of 14. Following procedure developed by Aggarwal[8] (supporting information, page S-11) a solution of furan (33 µL, 450 µmol, 1.2 eq.) in THF (1.5 mL) was cooled to –78 ˚C and treated with *n*-BuLi (0.2 mL, 450 µmol, 1.2 eq., 2.25 M in hexanes). The cooling bath was removed and the mixture was stirred at room temperature for 1 h. The mixture was cooled to –78 ˚C and (*S*)-**7j** (126 mg, 367 µmol) was added dropwise as a solution in THF (0.8 mL). The mixture was stirred at –78 ˚C for 1 h and a solution of NBS (80.3 mg, 450 µmol, 1.2 eq.) in THF (1.5 mL) was added dropwise. After 1 h at –78 ˚C, $Na_2S_2O_3$ sat (1.5 mL) was added and the reaction mixture was allowed to warm to room temperature. The reaction mixture was diluted with Et_2O (15 mL) and brine (10 mL). The layers were separated and the aqueous layer was extracted with Et_2O (3 × 15 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under vacuum. The crude material was purified by flash chromatography on silica gel (5:95 EtOAc/hexanes) to give (*S*)-**14** (54.4 mg, 52%): TLC analysis (50:50 DCM/hexanes) R_f 0.5; $[\alpha]_D$ = +33.8° (c = 1.5, $CHCl_3$); chiral HPLC analysis (Chiralpak-IC, 97:3 hexanes:isopropanol @ 1.0 mL/min) showed peaks at 5.07 (*R*-enantiomer, 7.1%) and 5.32 min (*S*-enantiomer, 92.9%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7. 41 (1H, dd, *J* = 1.8 & 0.9 *Hz,* o), 7.33-7.18 (5H, m, aryl), 6.35 (1H, dd, *J* = 3.15 & 1.95 *Hz*, n), 6.15 (1H, dd, *J* = 3.15 & 0.75 *Hz*, m), 4.24 (2H, s, c), 2.61-2.42 (2H, m, g), 2.16-1.92 (2H, m, f), 1.89 (3H, s, a'), 1,87 (3H, s, a), 1.44 ppm (3H, s, e); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.42 (l), 154.65 (b), 142.97 (h), 141.08 (aryl), 128.42 (aryl), 128.40 (aryl), 125.73 (aryl), 109.90 (n), 105.18 (m), 79.42 (c), 40.81 (d), 39.49 (f), 30.82 (g), 21.85 (a'), 21.64 (e), 15.72 ppm (a); IR (neat) 3029 (C-H aromatic stretching), 2930 (C-H aliphatic stretching), 1603 (C=C stretching), 1454 (C=N stretching), 1072 (C-O stretching), 920 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{18}H_{23}NO_2$ (M + Na): 308.1618, found: 308.1618 *m/z.*



Coupling with vinyl ethyl ether: synthesis of 15. Following procedure developed by Aggarwal[8] (supporting information, page S-24) freshly distilled (under CaH_2) vinyl ethyl ether (133 µL, 1.39 mmol) was dissolved in anhydrous THF (4.0 mL) under a nitrogen atmosphere and cooled to −78 ˚C. tBuLi (1.65 M in pentane, 530 µL, 870 µmol) was added dropwise over 5 min. The reaction mixture was stirred for 30 min at −78 ˚C, then placed in a −20 ˚C cooling bath (ice/NaCl), stirred for 30 min, and then re-cooled to −78 ˚C. To the resulting bright yellow solution was added tertiary boronic ester (*S*)-**7j** (120 mg, 347 µmol) in THF (2.0 mL) dropwise over 5

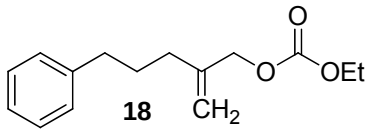
min. The reaction mixture was stirred for 30 min at −78 ˚C, then placed in a −20 ˚C cooling bath (ice/NaCl), stirred for 10 min, and then re-cooled to −78 ˚C. To the resulting pale yellow solution, was added dropwise a solution iodine (353 mg, 1.39 mmol) in THF (4.0 mL) over 15 min. The reaction mixture was stirred for 30 min at −78 ˚C, then at ambient temperature for 5 min, and then re-cooled to −78 ˚C. A suspension of NaOMe (150 mg, 2.78 mmol) in MeOH (4.0 mL) was added. The cooling bath was removed and the reaction mixture stirred for 1 h at ambient temperature before the addition of HCl (aq) (2 M, 3.0 mL). The reaction mixture was stirred for 15 min at ambient temperature. Saturated $Na_2S_2O_3$ (aq) (5.0 mL) was added and the reaction stirred for 1 h. The reaction was diluted with diethyl ether (15 mL) and the layers separated. The aqueous phase was extracted with diethyl ether (3 × 15 mL). The combined organic phases were washed with brine and dried over $MgSO_4$. The solvent removed in vacuo and the crude material purified by flash chromatography (5:95 EtOAc/Hex) to give (*S*)-**15** (36.2 mg, 40%) as a colorless oil. TLC analysis (90:10 DCM/hexanes) R_f 0.5; $[\alpha]_D$ = +20.5˚ (c = 1.0, $CHCl_3$); chiral HPLC analysis (Chiralpak-IC, 90:10 hexanes:isopropanol @ 1.0 mL/min) showed peaks at 12.1 (*R*-enantiomer, 7.0%) and 12.57 min (*S*-enantiomer, 93.0%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33-7.28 (2H, m, aryl), 7.23-7.17 (3H, m, aryl), 4.27 (1H, d, *J* = 10.2 *Hz,* c), 4.11 (1H, d, *J* = 10.2 *Hz,* c'), 2.65-2.43 (2H, m, g), 2.23 (3H, s, m), 2.00-1.87 (1H, m, f), 1.84 (3H, s, a) 1.82 (3H, s, a') 1.82-1.73 (1H, m, f'), 1.27 ppm (3H, s, e); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.75 (l), 155.33 (b), 142.19 (h), 128.58 (i), 128.40 (j), 126.08 (k), 78.52 (c), 52.28 (d), 37.59 (f), 30.60 (g), 26.07 (m), 21.82 (a'), 19.22 (e), 15.74 ppm (a); IR (neat) 2920 (C-H aliphatic stretching), 1707 (C=O stretching), 1455 (C=N stretching), 1073 (C-O stretching), 920 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{16}H_{23}NO_2$ (M + Na): 284.1626, found: 284.1612 *m/z.*

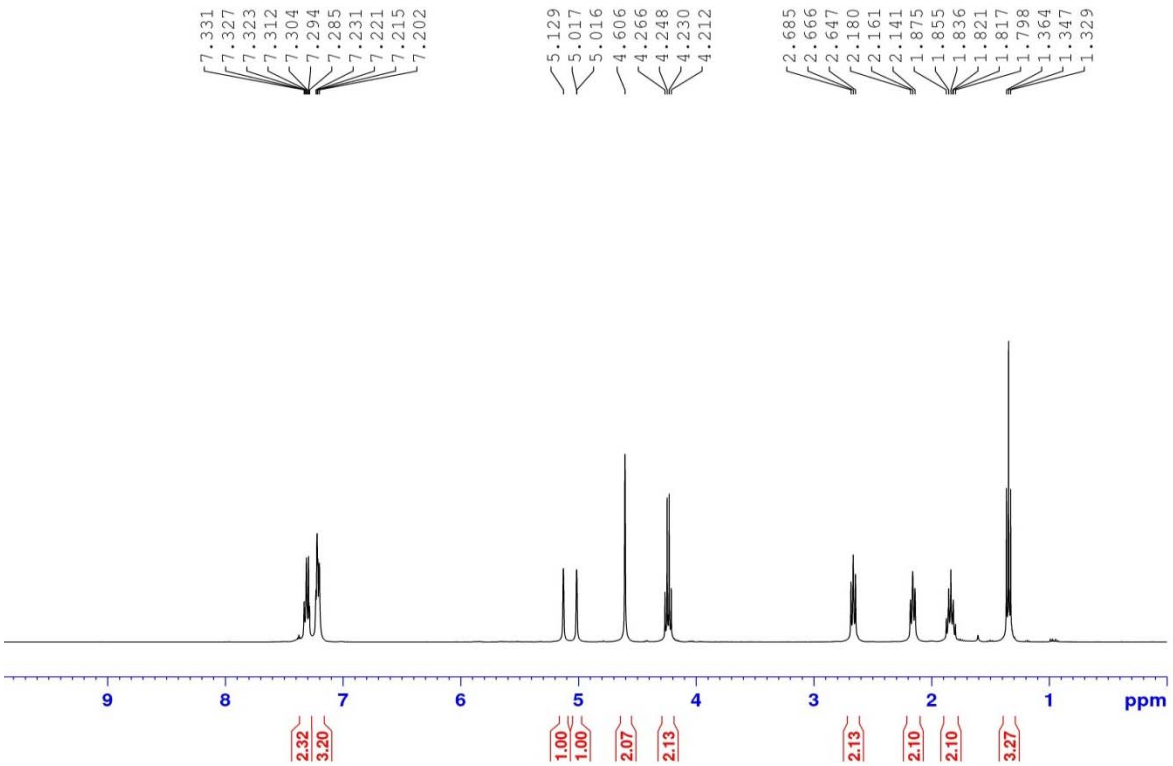
*[**Note:** 50% of starting material was recovered; ketone **15** partially underwent cyclization with formation of isooxazoline **16** due to presence of HCl. Cyclization can be avoided using NH_4Cl instead of HCl.]*



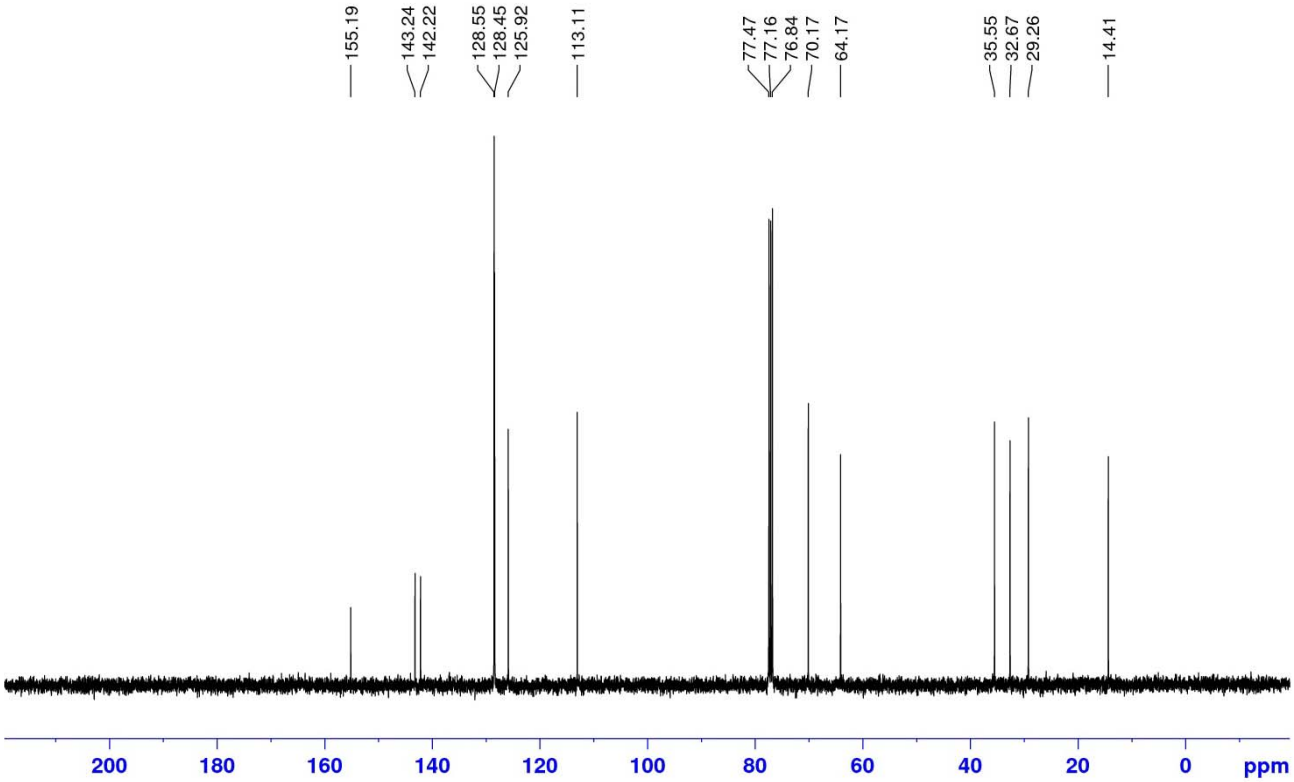
Synthesis of 3,4,4-trisubstituted isoxazoline 16. Ketone (*S*)-**15** (22.0 mg, 84.0 μmol) was dissolved in a mixture of MeOH (150 μL), H_2O (150 μL) and HCl (150 μL) and was stirred in open flask at 40 ˚C overnight. Solvents were removed under reduced pressure, ethyl acetate (2.0 mL) was added. The organics were washed with sodium bicarbonate, brine, dried with Na_2SO_4 and concentrated under reduced pressure. Crude material was purified by flash chromatography (10:90 EtOAc/Hex) to give (*R*)-**16** as a clear colorless oil (15.0 mg, 88%): TLC analysis (80:20 EtOAc/Hex) R_f 0.5; $[\alpha]_D$ = -79.4˚ (c = 0.5, $CHCl_3$); chiral HPLC analysis (Chiralpak-IC, 70:30 hexanes:isopropanol @ 1.0 mL/min) showed peaks at 33.76 (*R*-enantiomer, 92.8%) and 37.37 min (*S*-enantiomer, 7.2%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.28 (2H, m, aryl), 7.25-7.18 (3H, m, aryl), 4.28 (1H, d, *J* = 8.1 *Hz,* a), 4. 01 (1H, d, *J* = 8.1 *Hz,* a'), 2.78-2.68 (1H, m, g), 2.51-2.40 (1H, m, g'), 1.93 (3H, s, d), 1.84-1.78 (2H, m, f), 1.29 ppm (3H, s, e); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.30 (c), 141.43 (h), 128.68 (i), 128.33 (j), 126.26 (k), 78.28 (a), 54.32 (b), 38.68 (f), 31.16 (g), 22.41 (e), 9.25 ppm (d); IR (neat) 2930 (C-H aliphatic stretching), 1455 (C=N stretching), 941 (C-O stretching), 852 cm^{-1} (N-O stretching); HRMS (ESI) calcd. for $C_{13}H_{17}NO$ (M + Na): 226.1222, found: 226.1222 *m/z.*

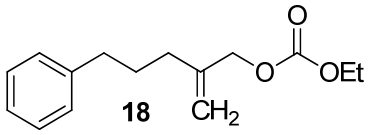
^{1}H NMR



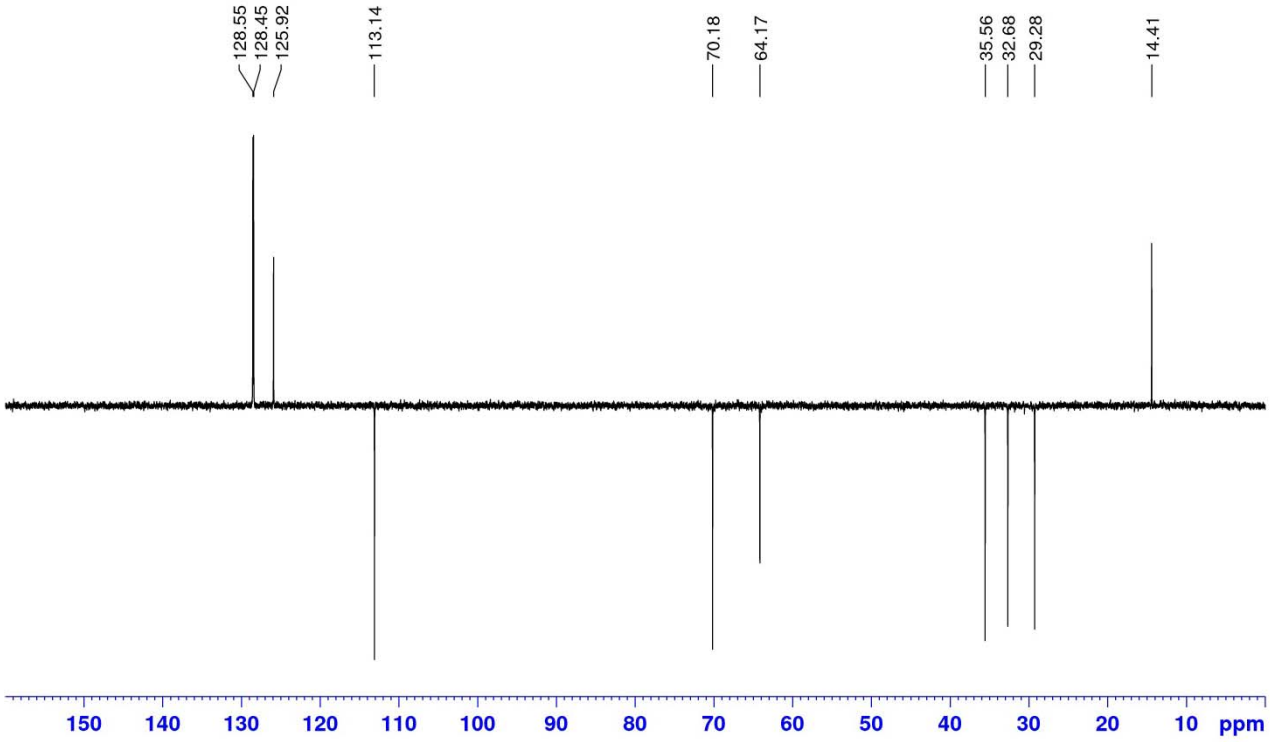


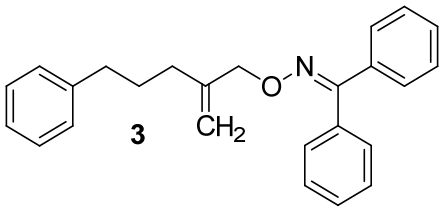
^{13}C NMR



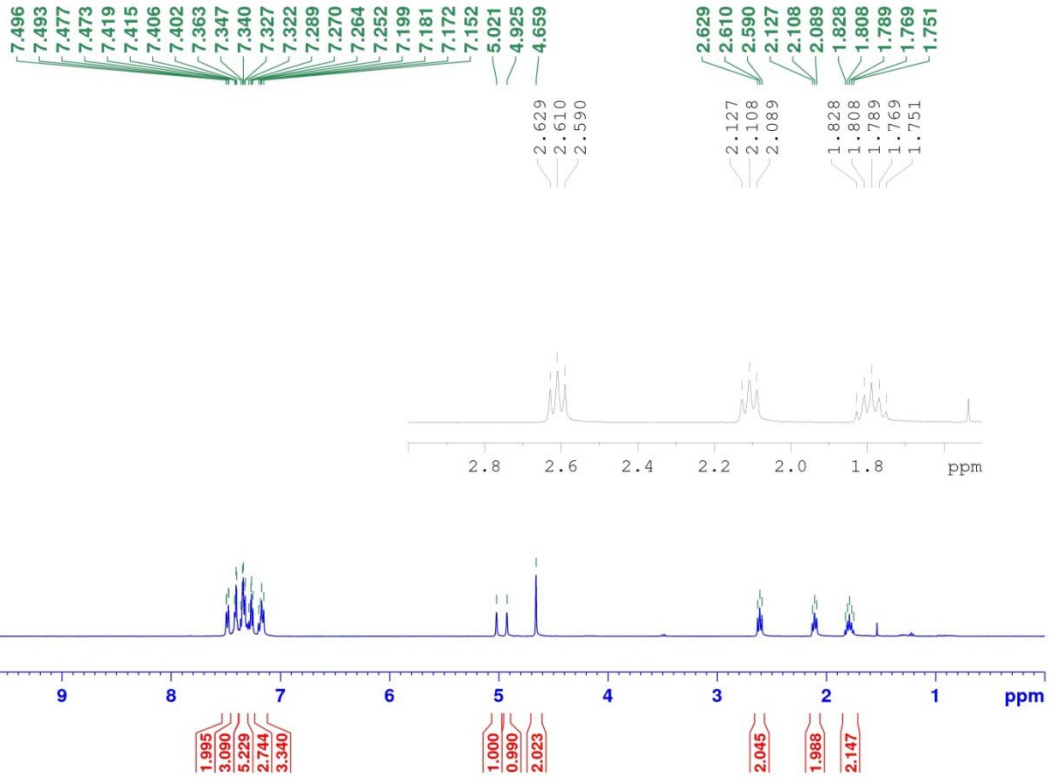


^{13}C DEPT135 NMR





^{1}H NMR



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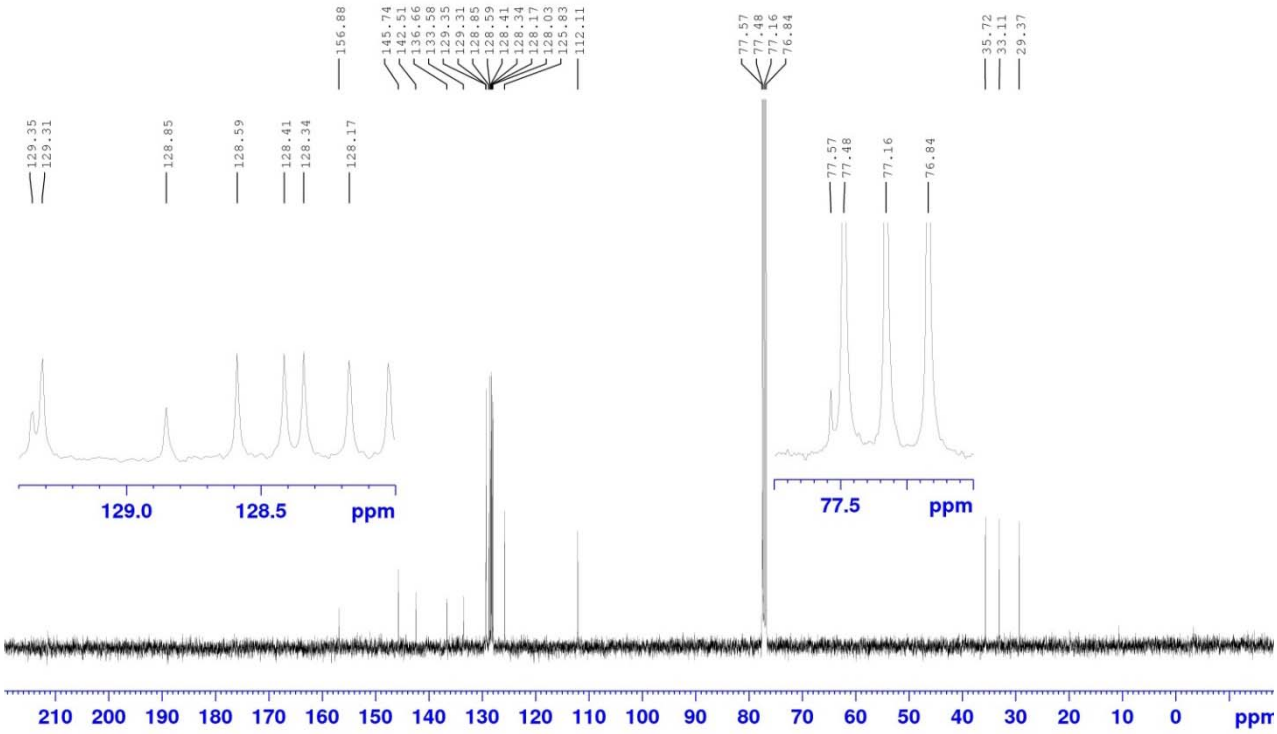

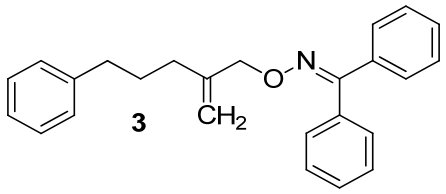

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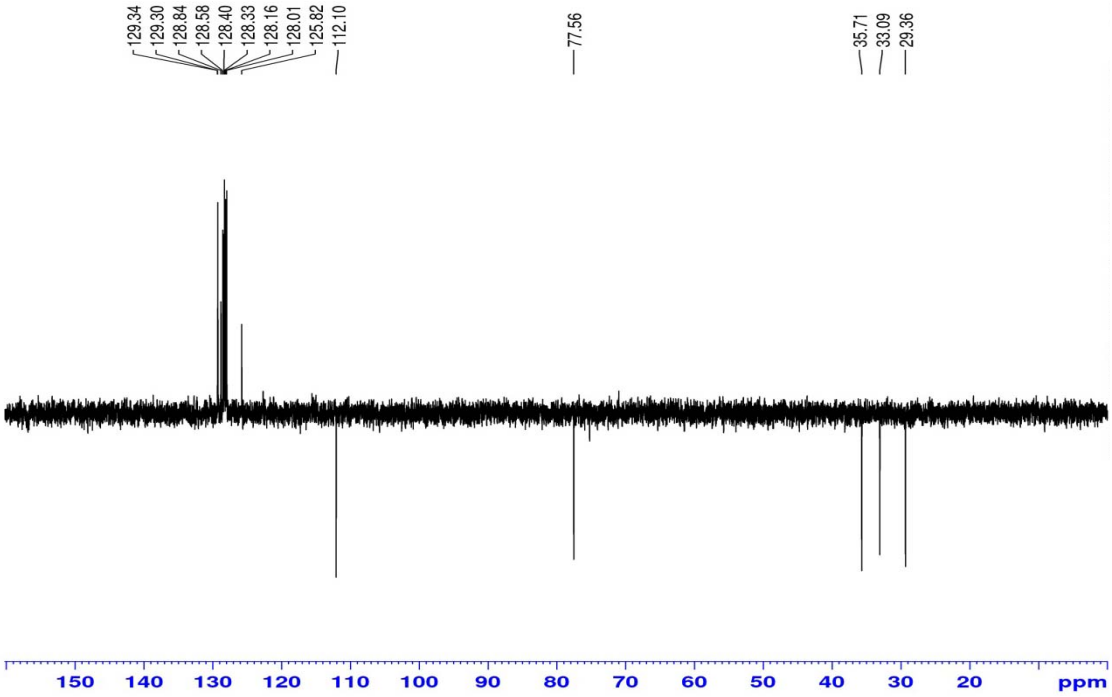

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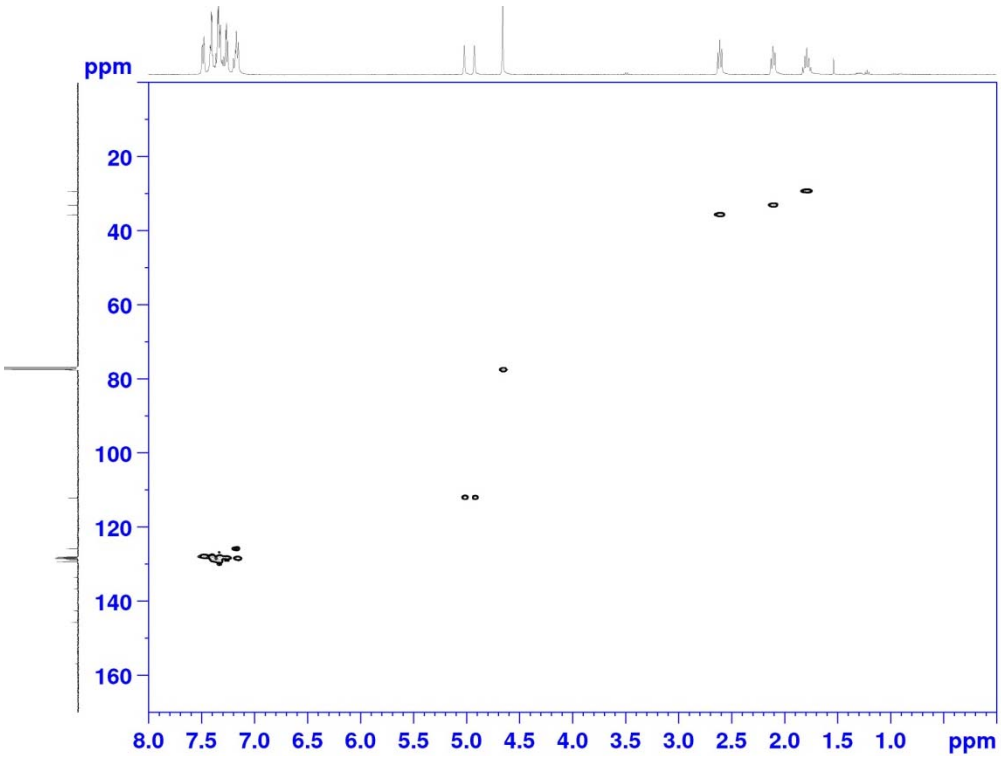

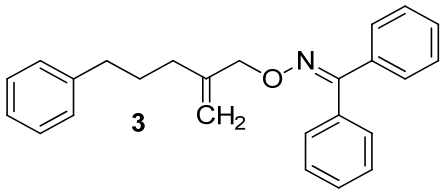

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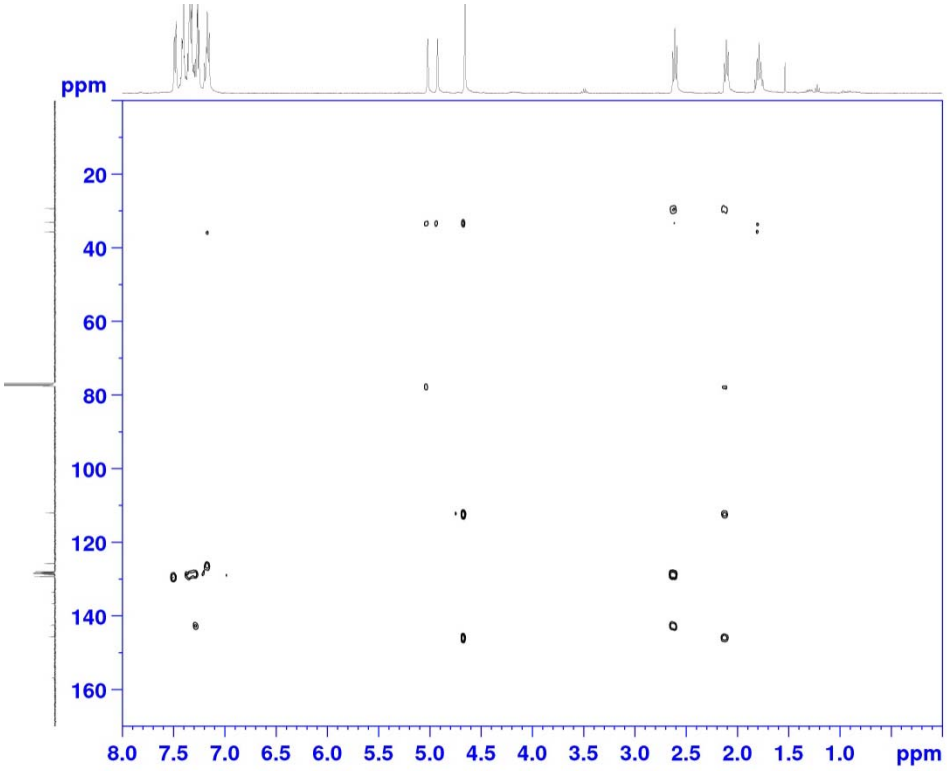

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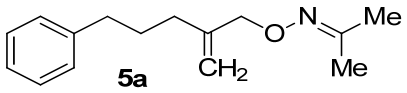

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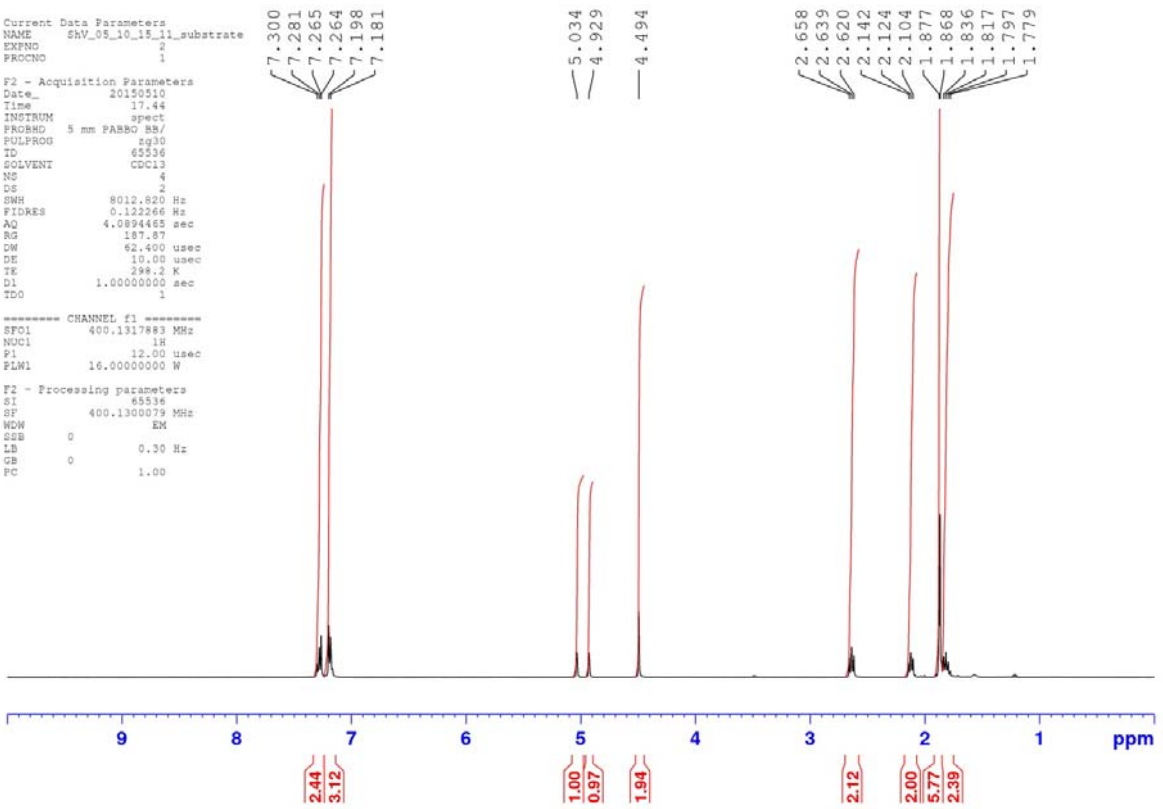
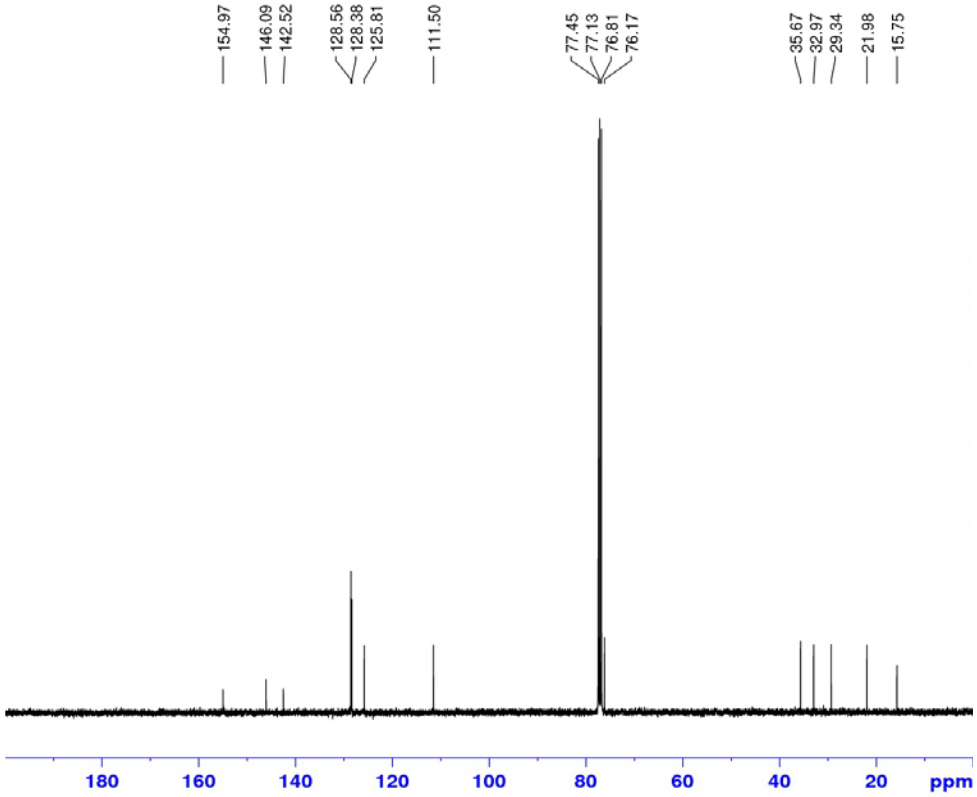
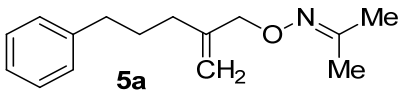


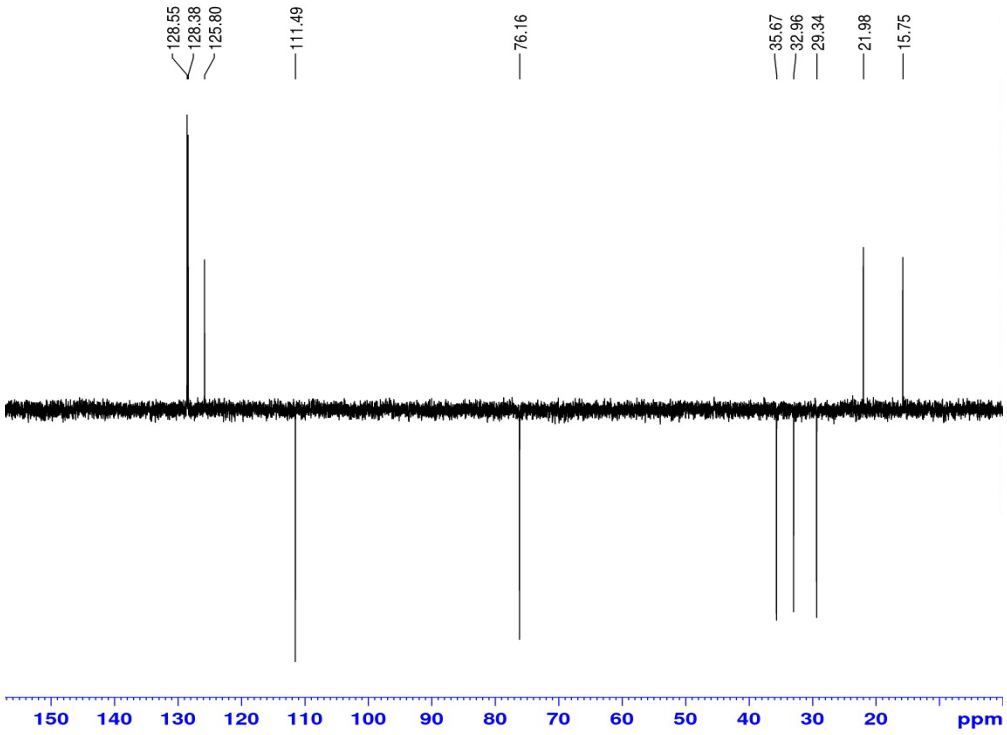
^{13}C NMR





5a

^{13}C DEPT135 NMR



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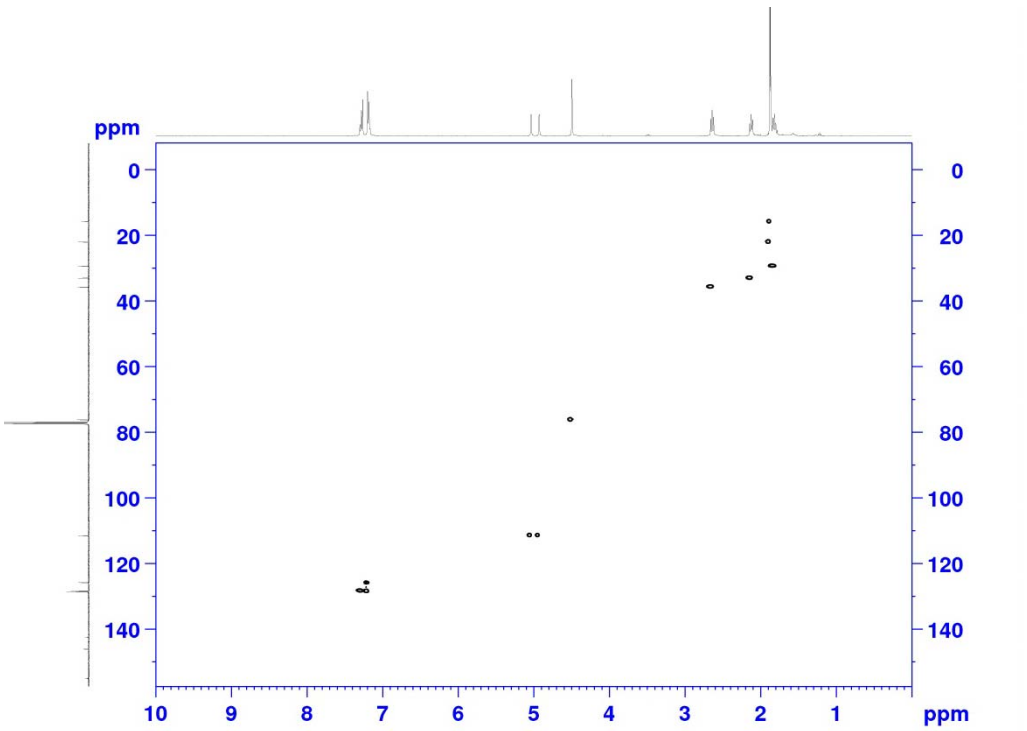

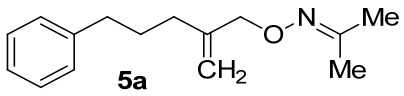

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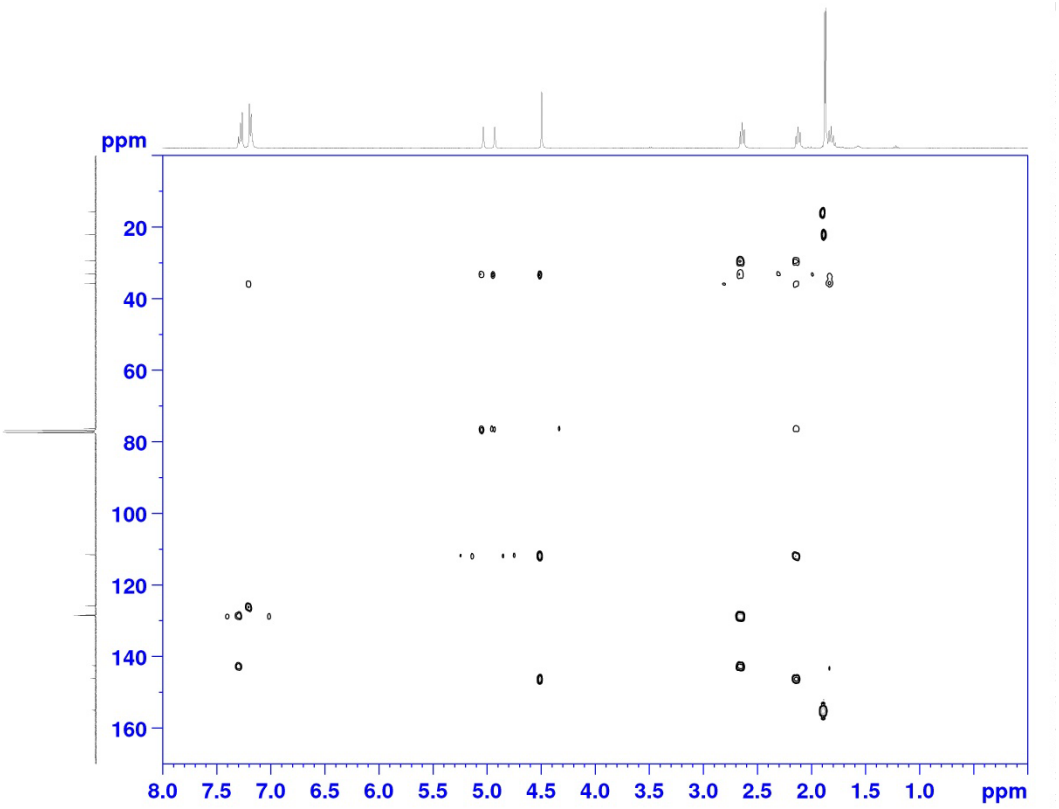
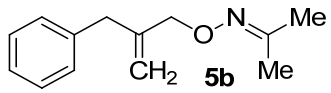


^{1}H NMR



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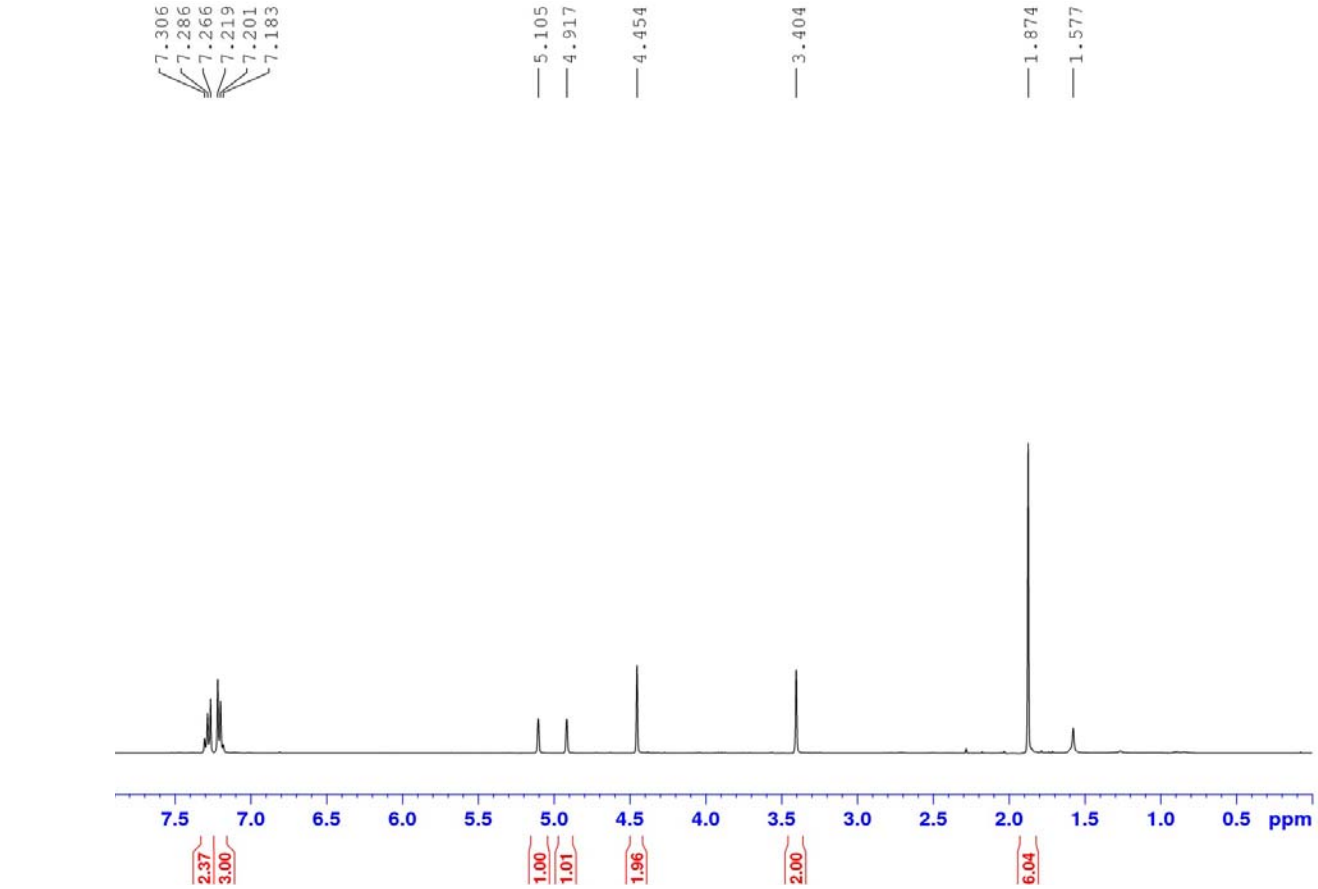

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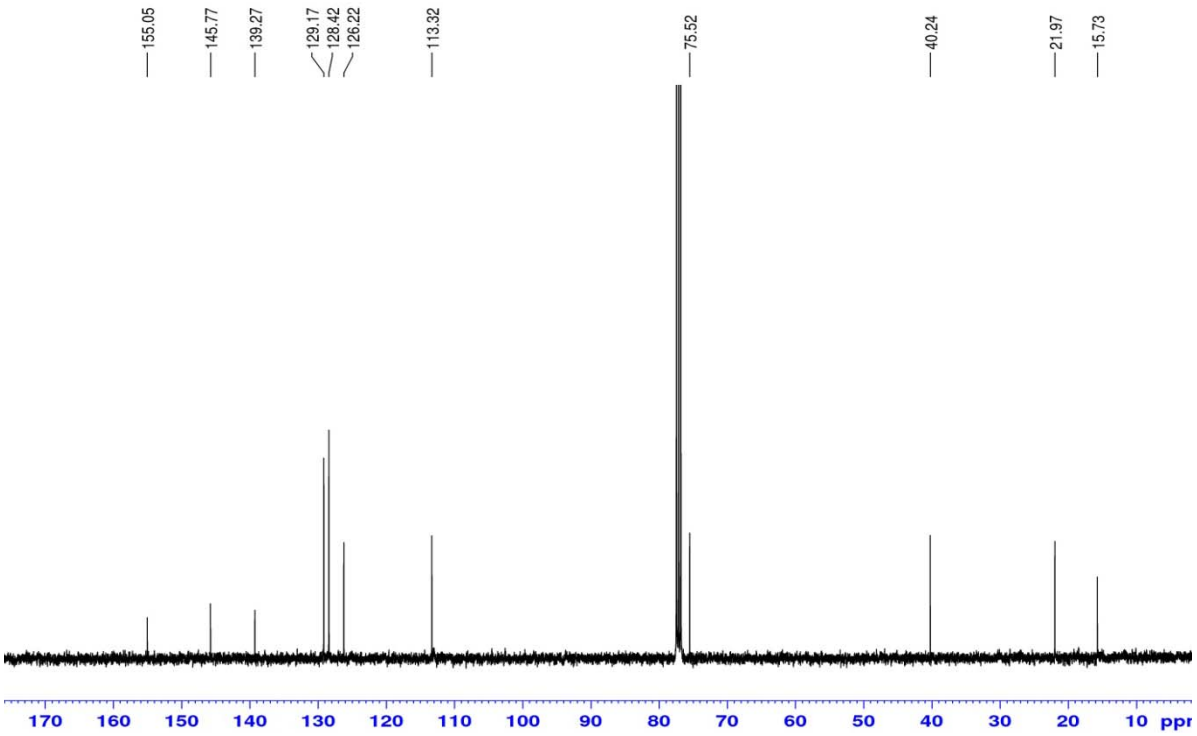
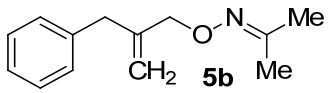


^{13}C DEPT 135 NMR



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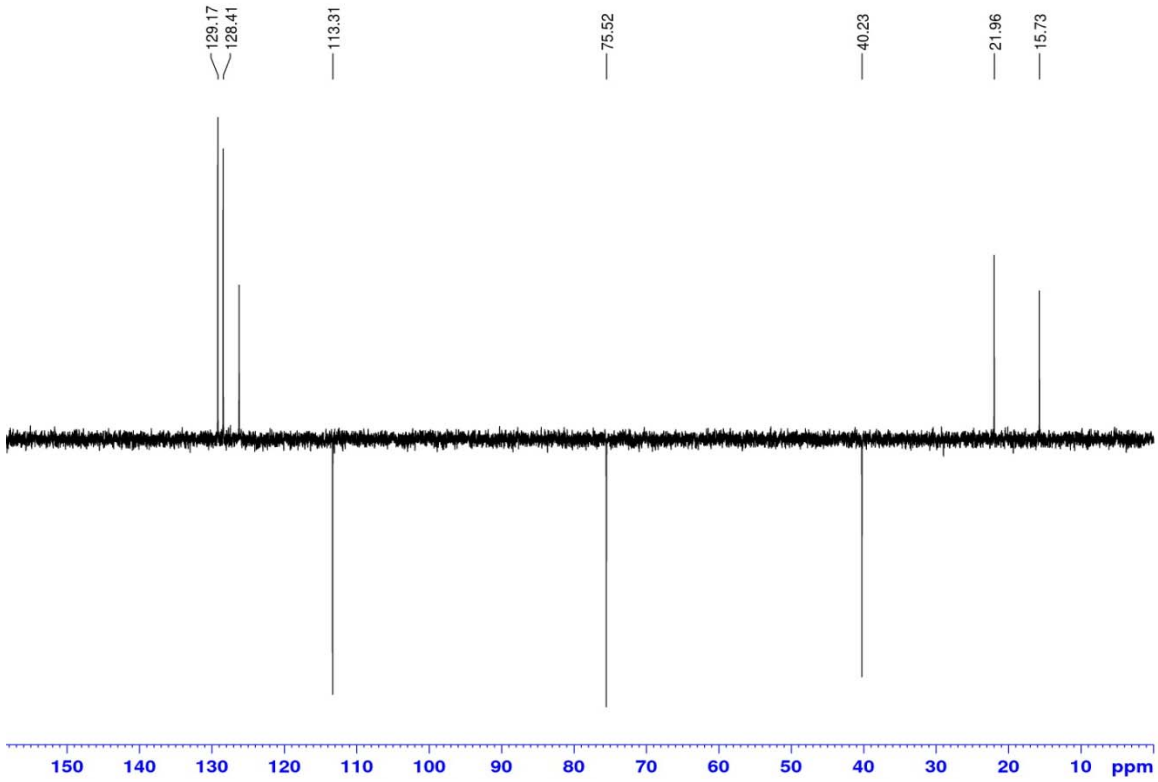

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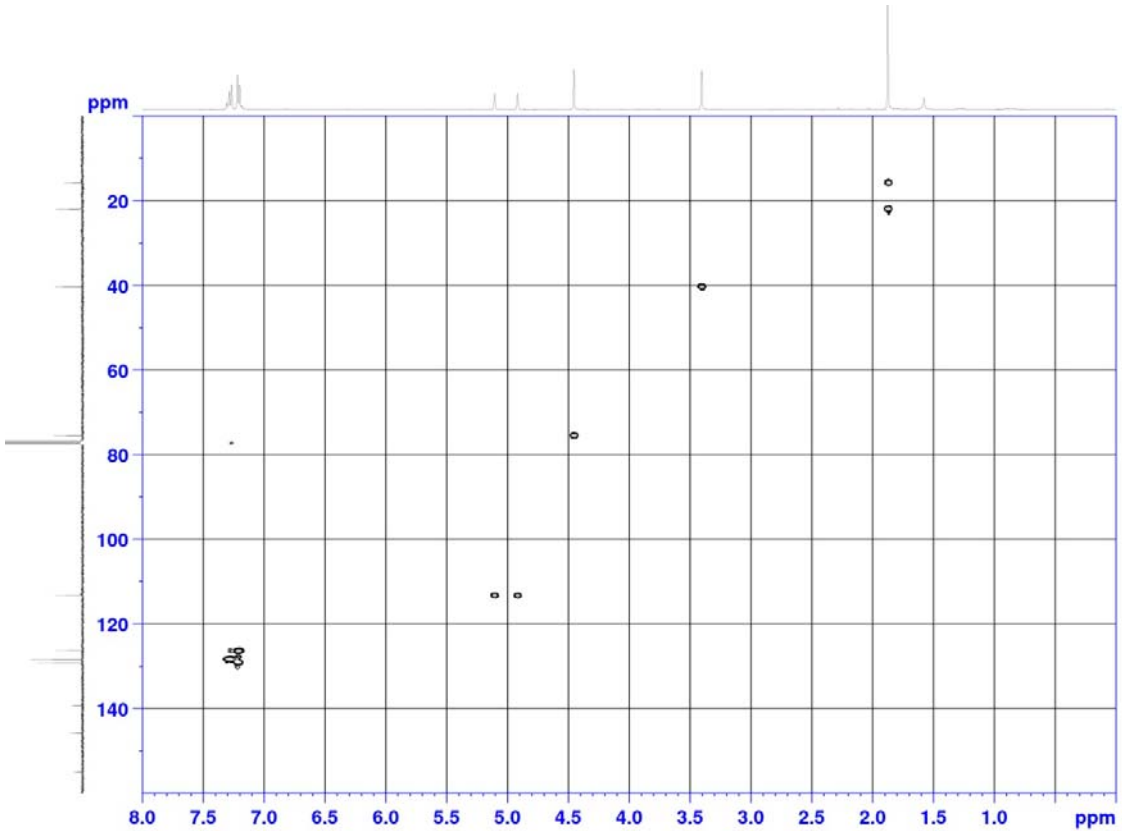

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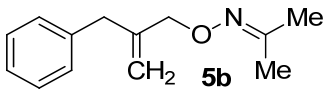

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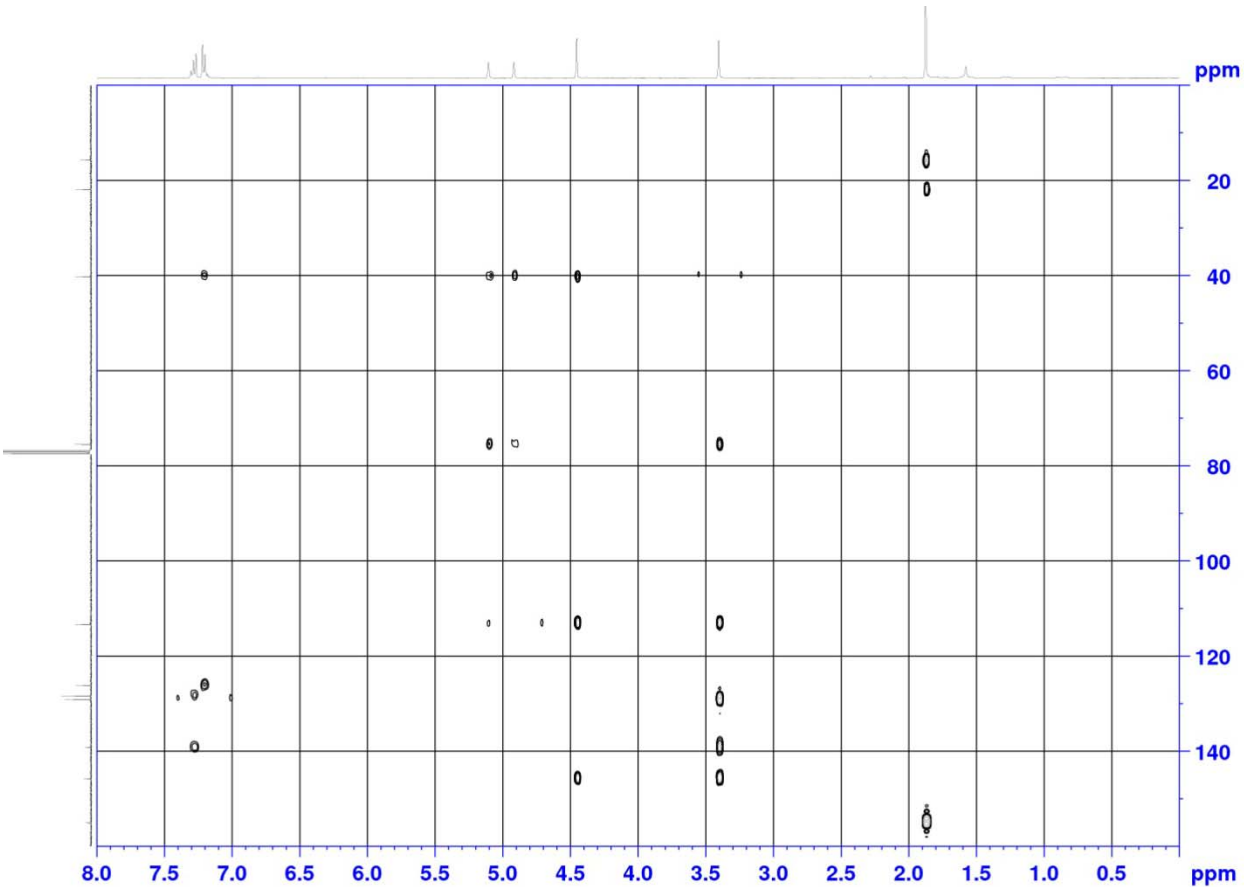

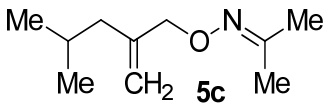

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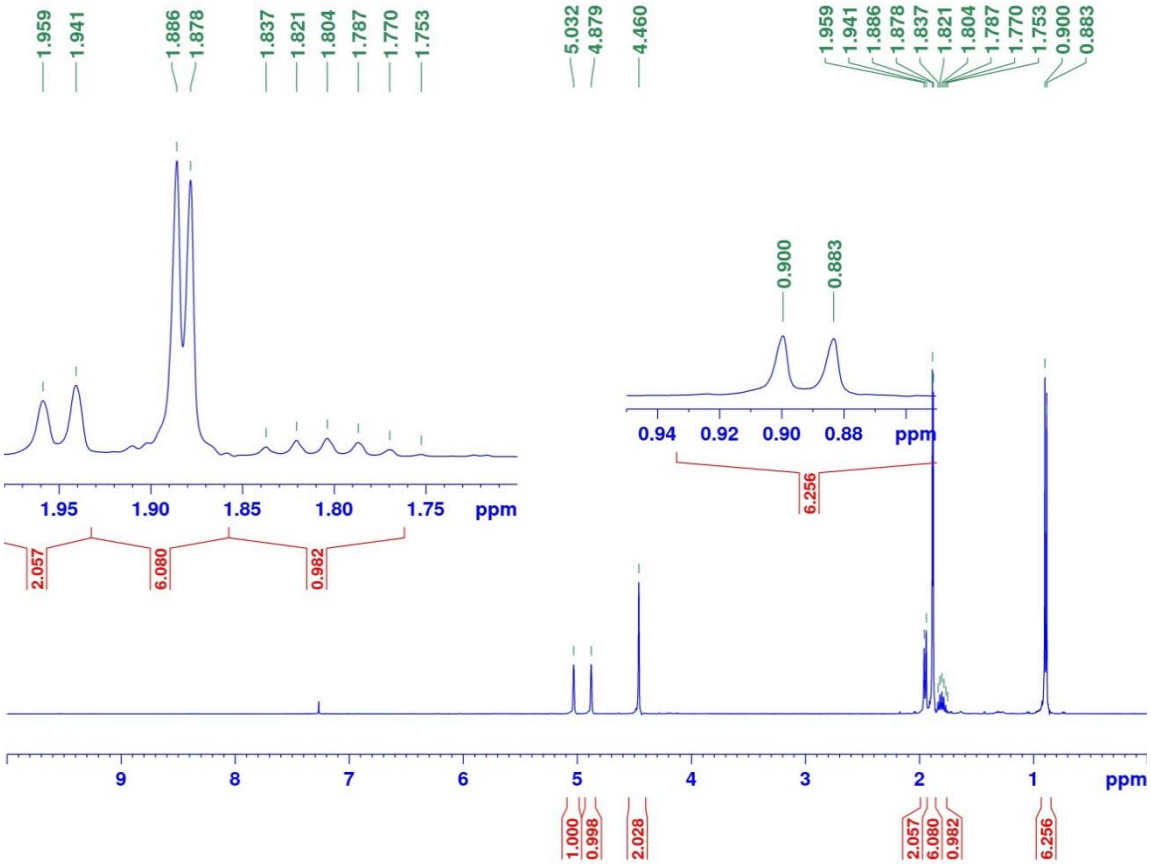

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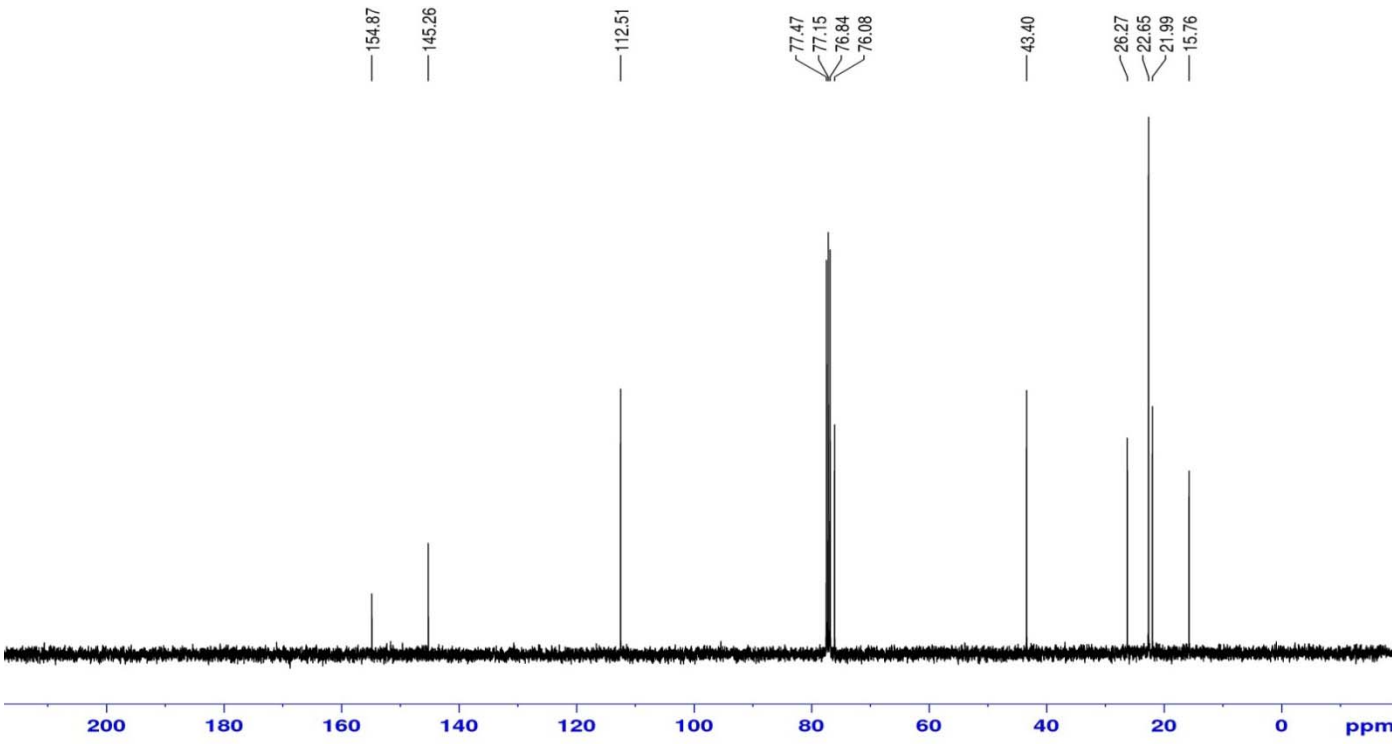

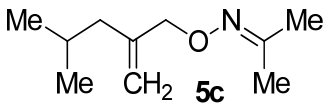

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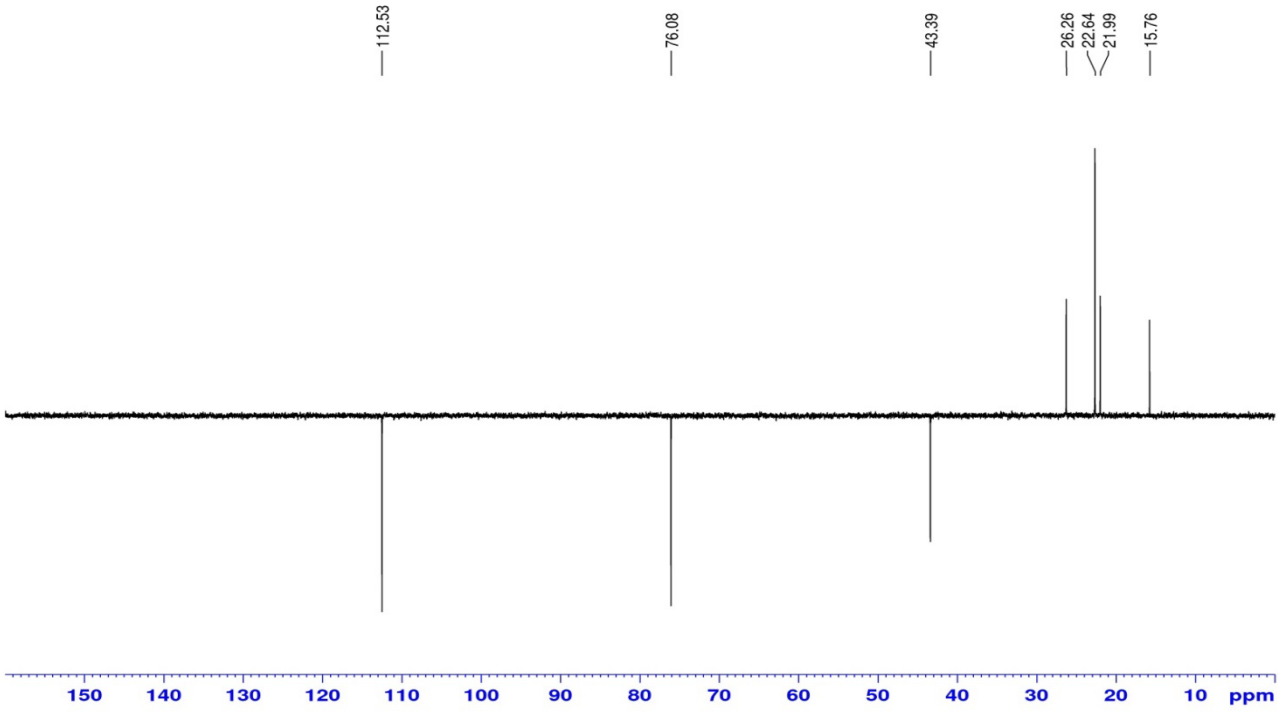
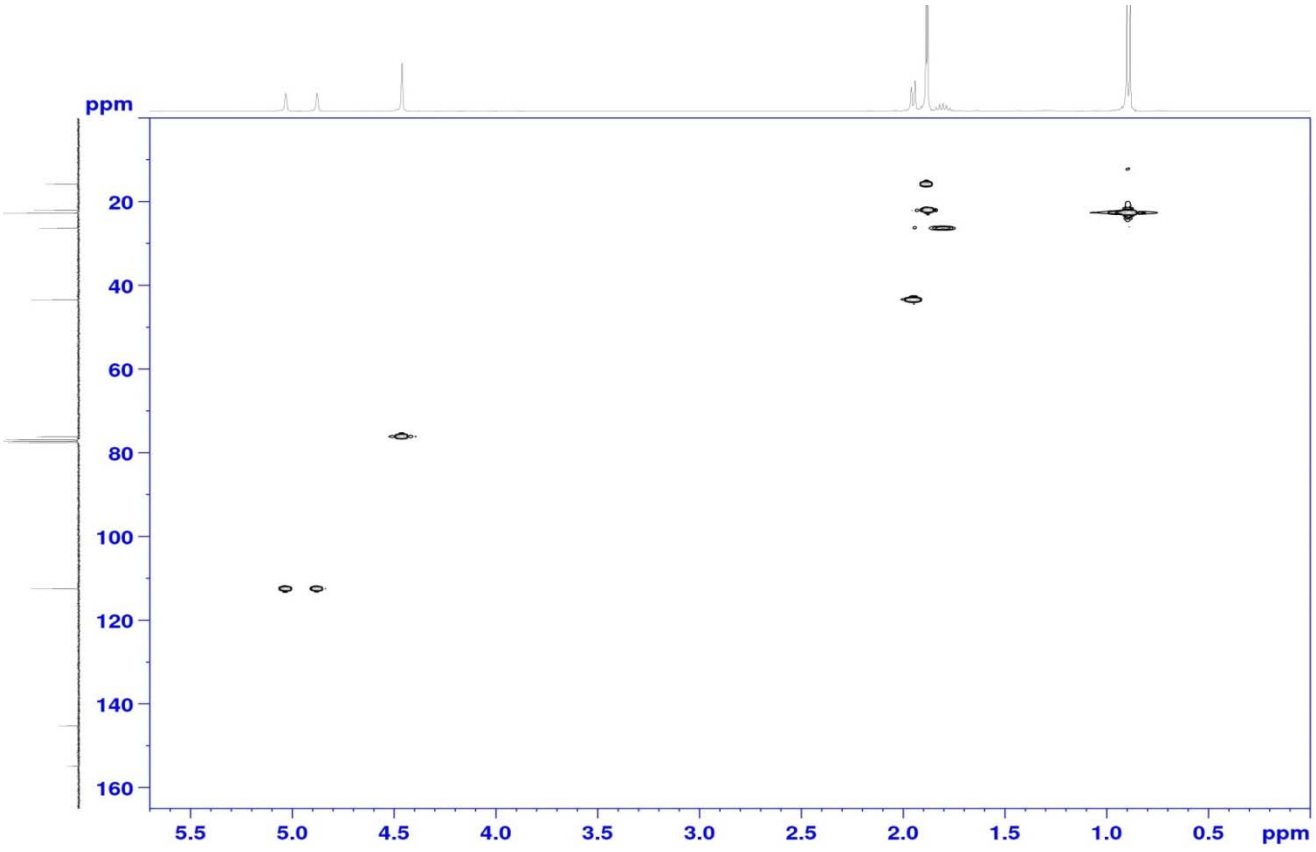


^{1}H-^{13}C HSQC NMR



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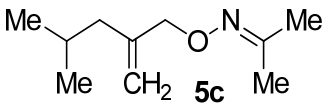

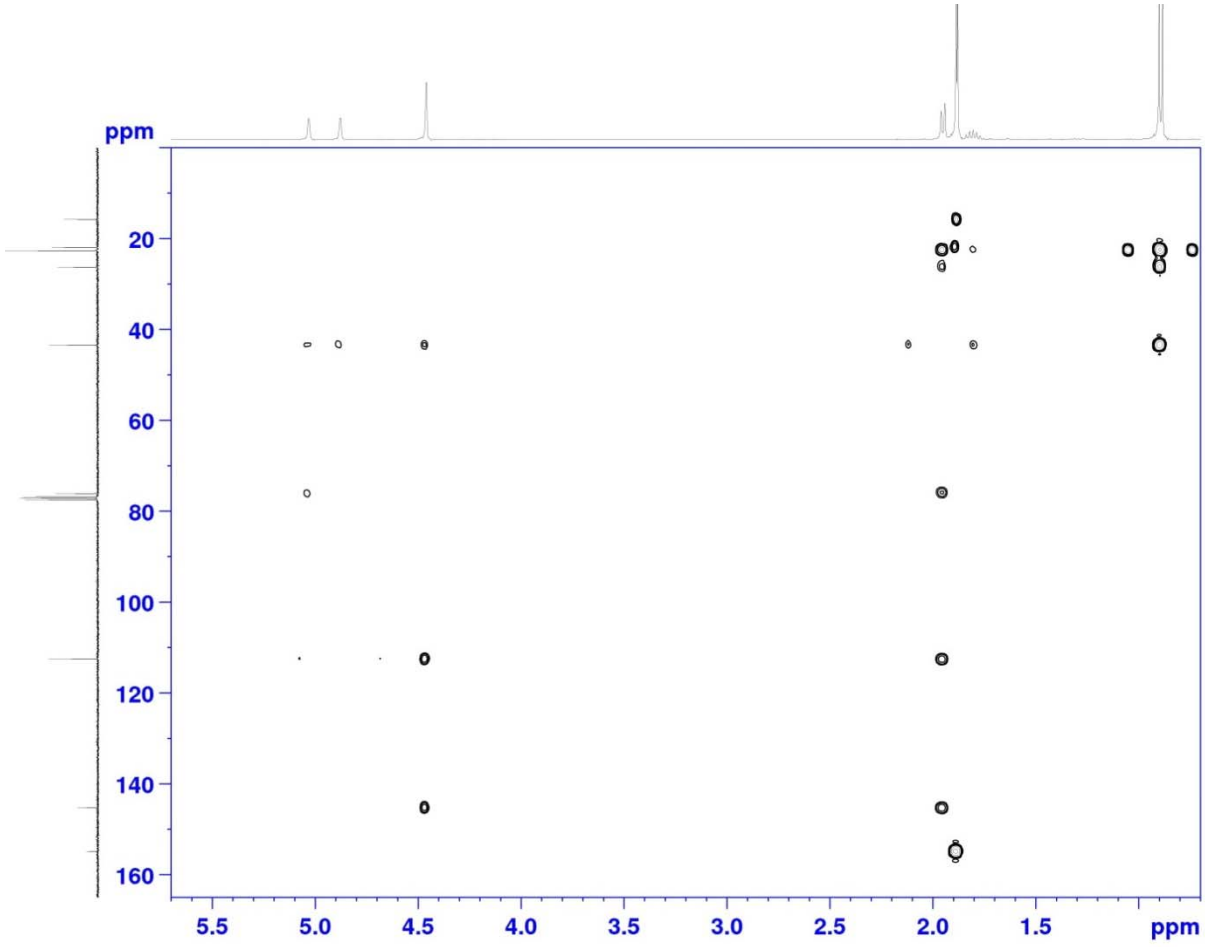

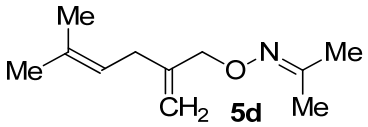

5d

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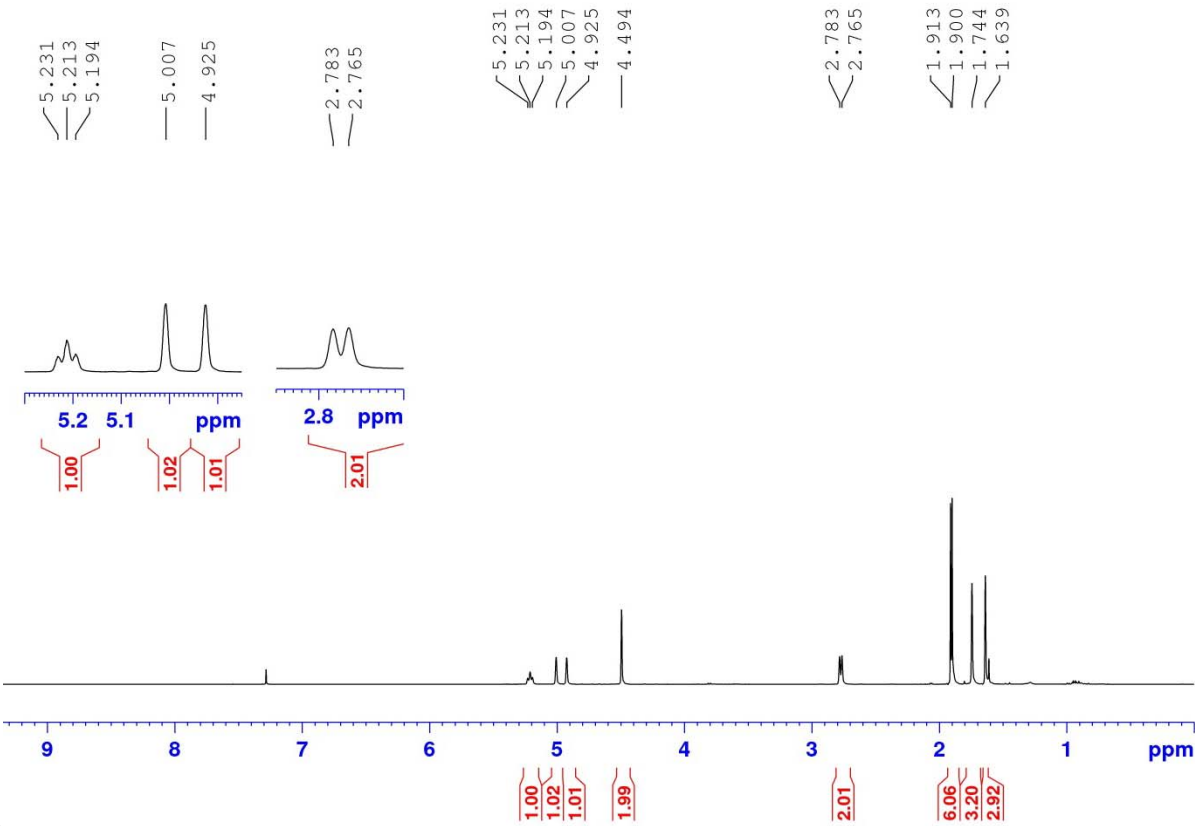

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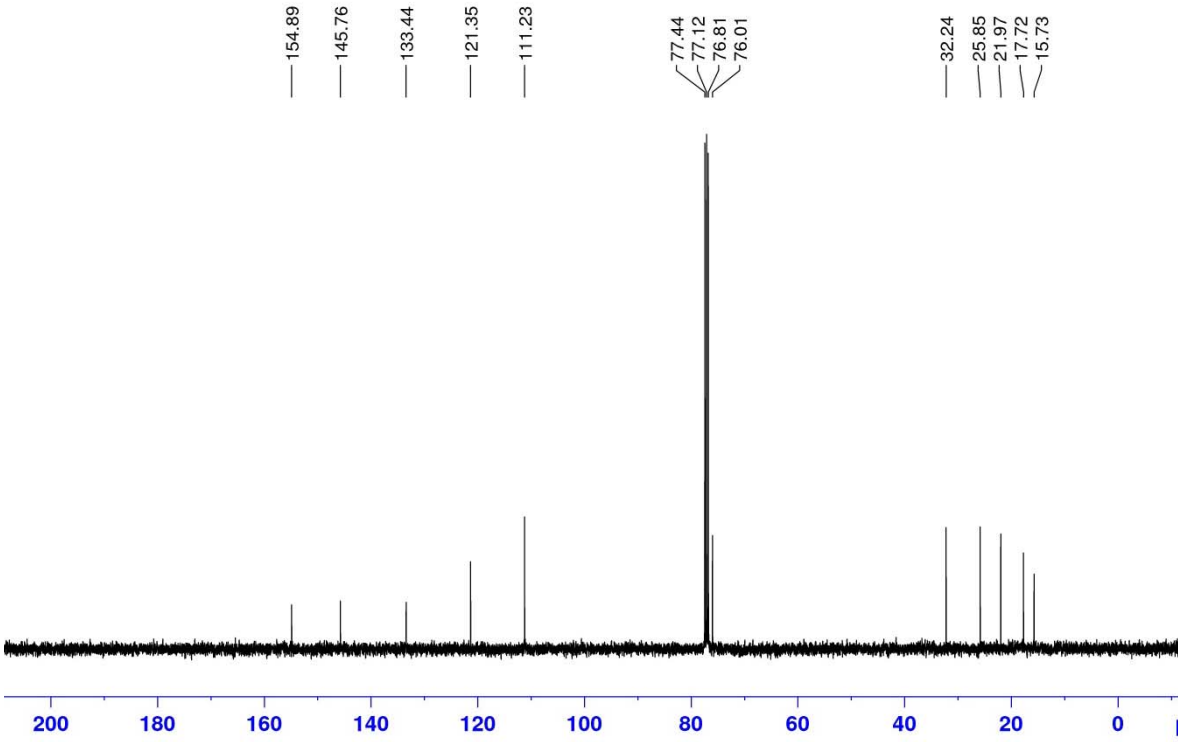

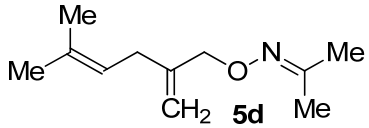

5d

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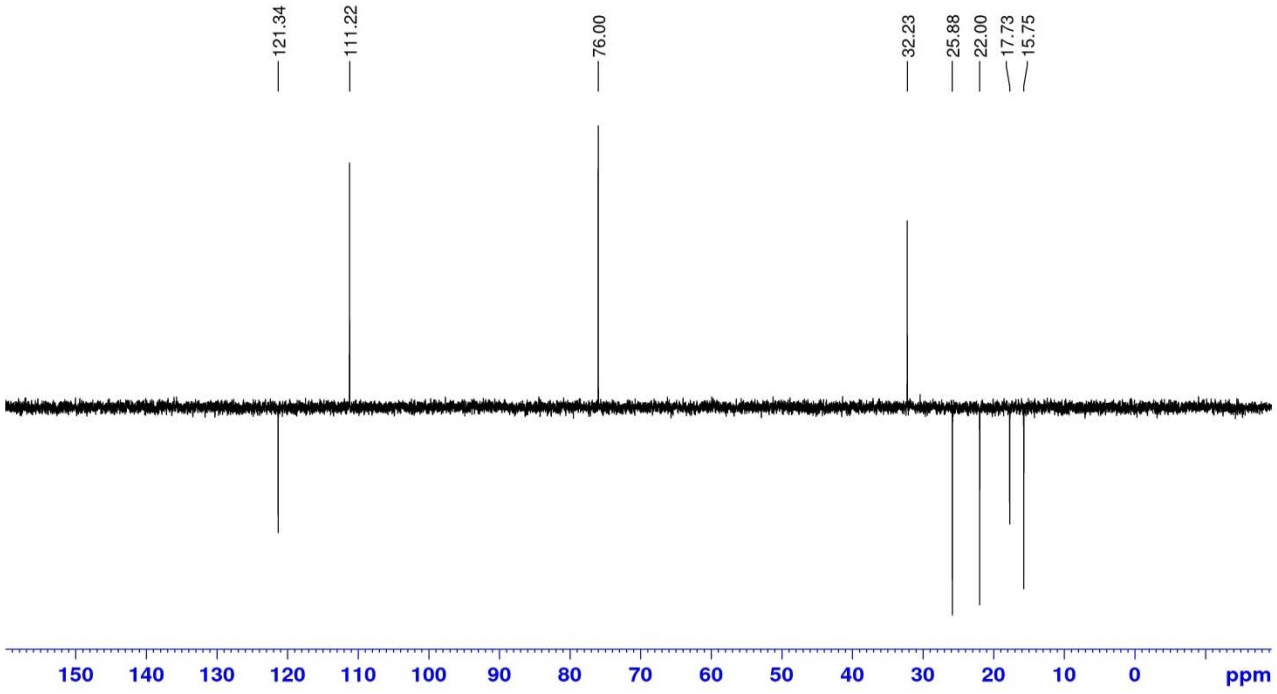
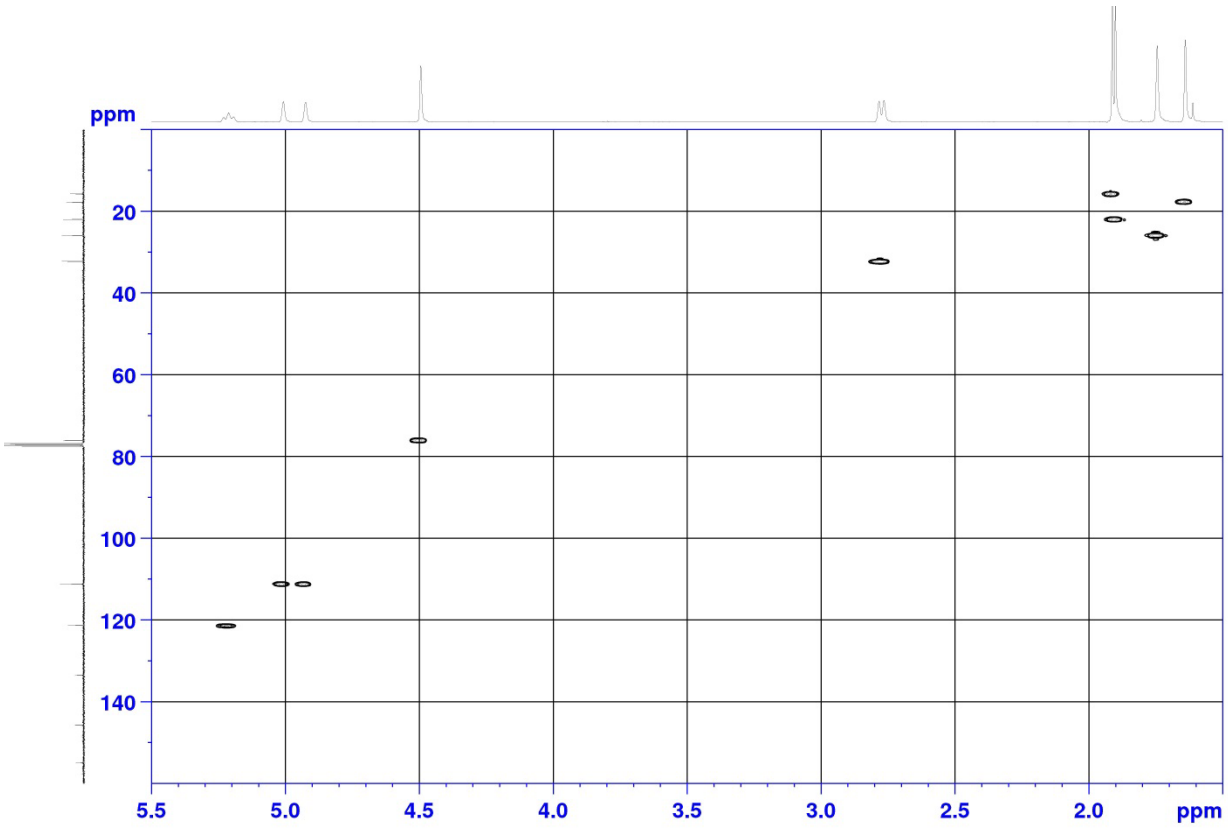


^{1}H-^{13}C HSQC NMR



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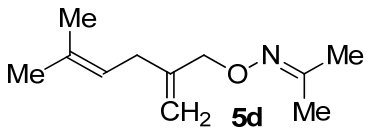
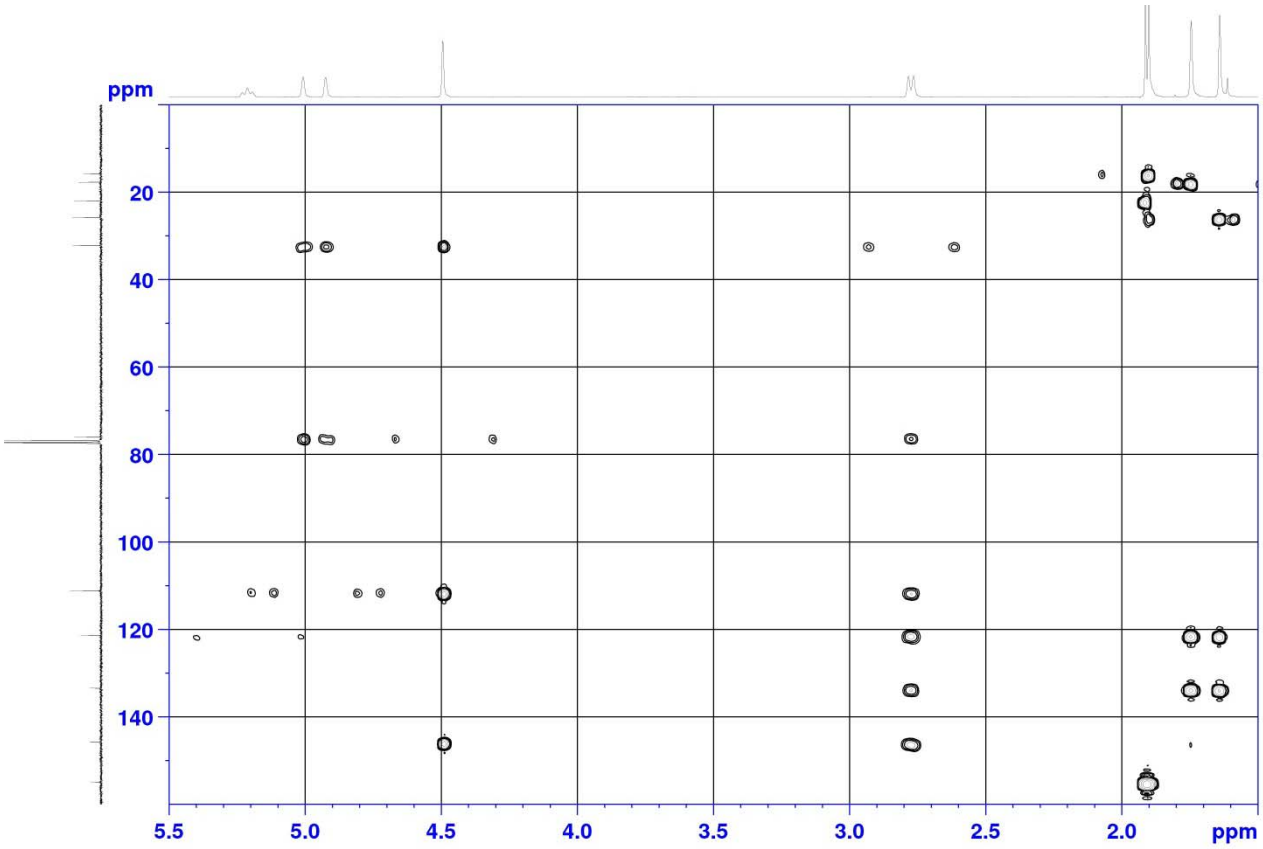
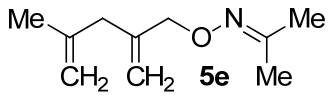
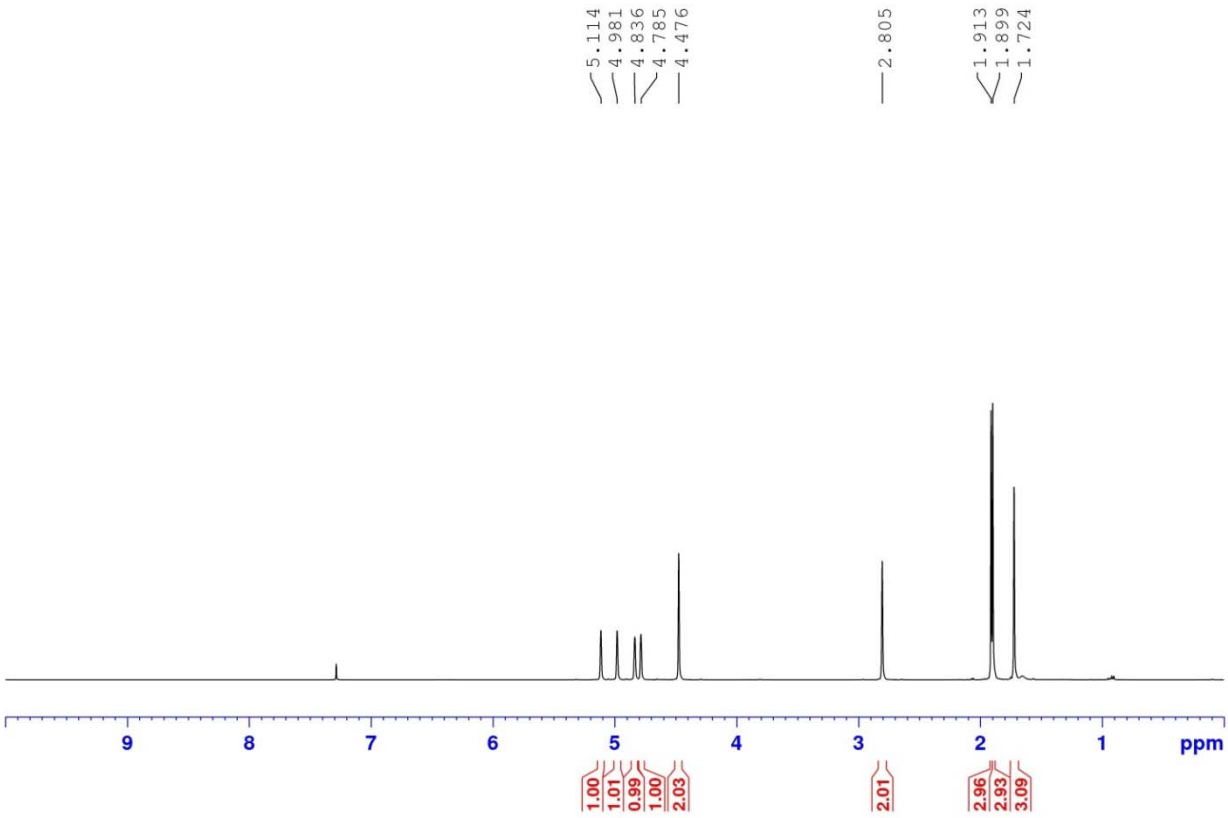


5d



^{1}H NMR





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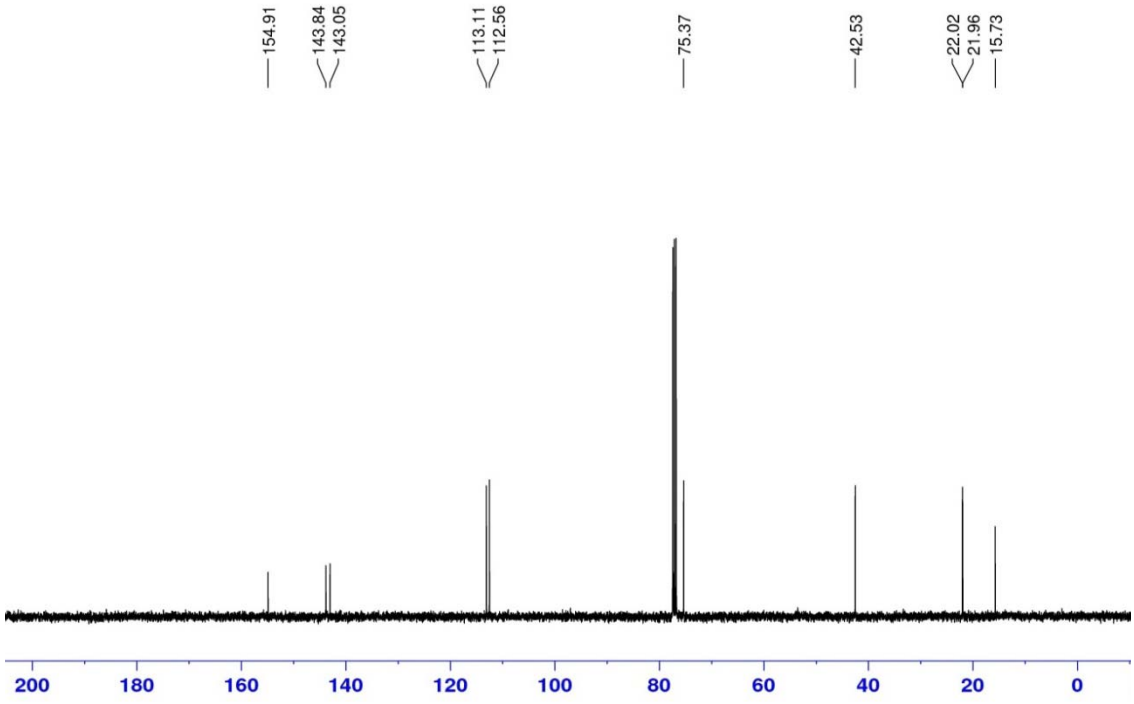

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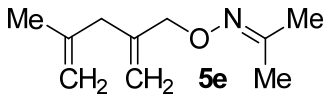
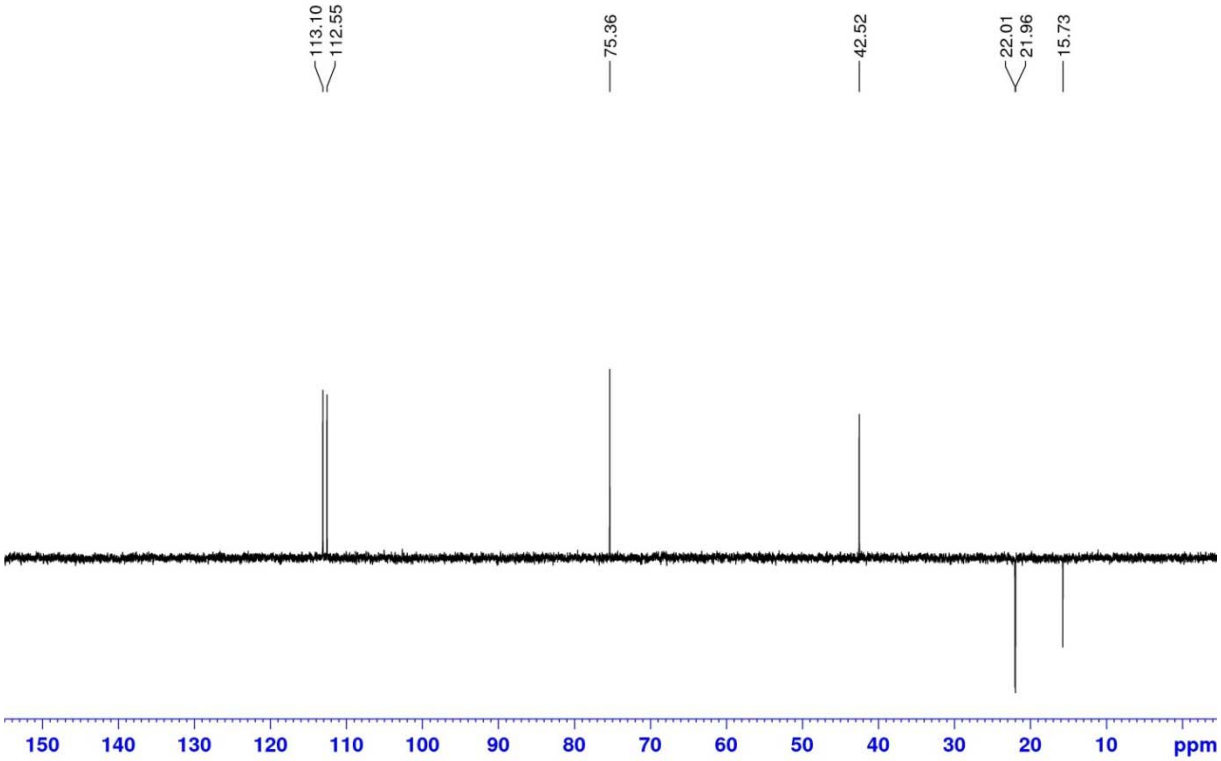
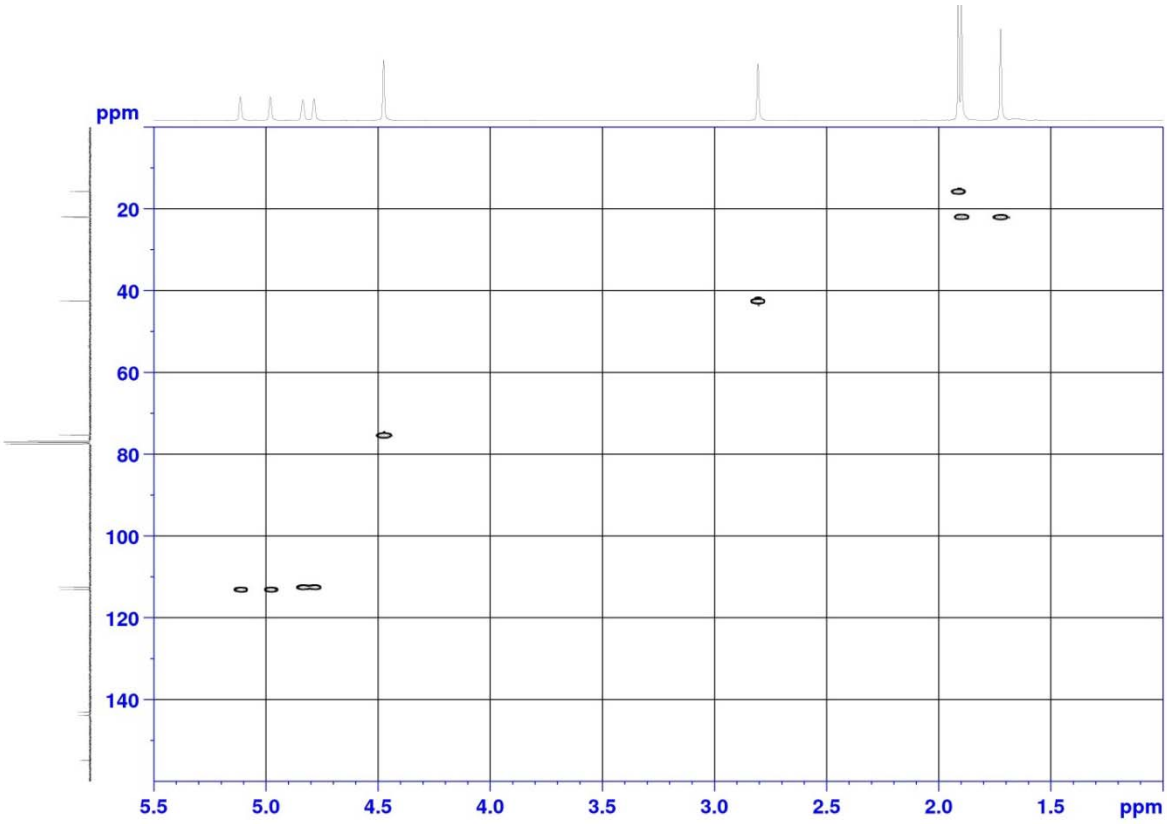
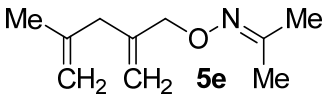


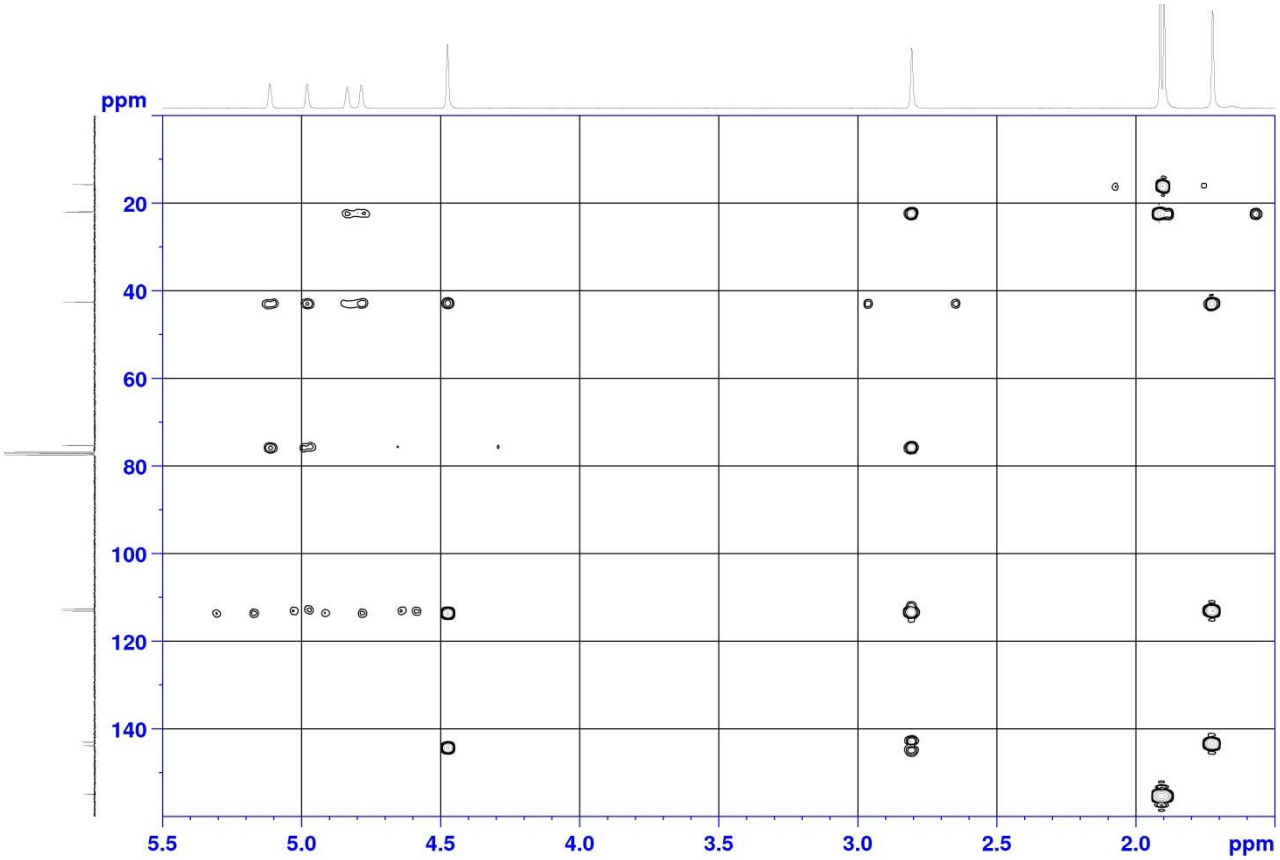


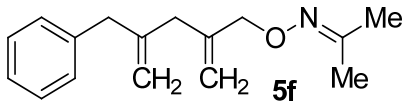
^{1}H- ^{13}C HSQC NMR



^{1}H- ^{13}C HMBC NMR







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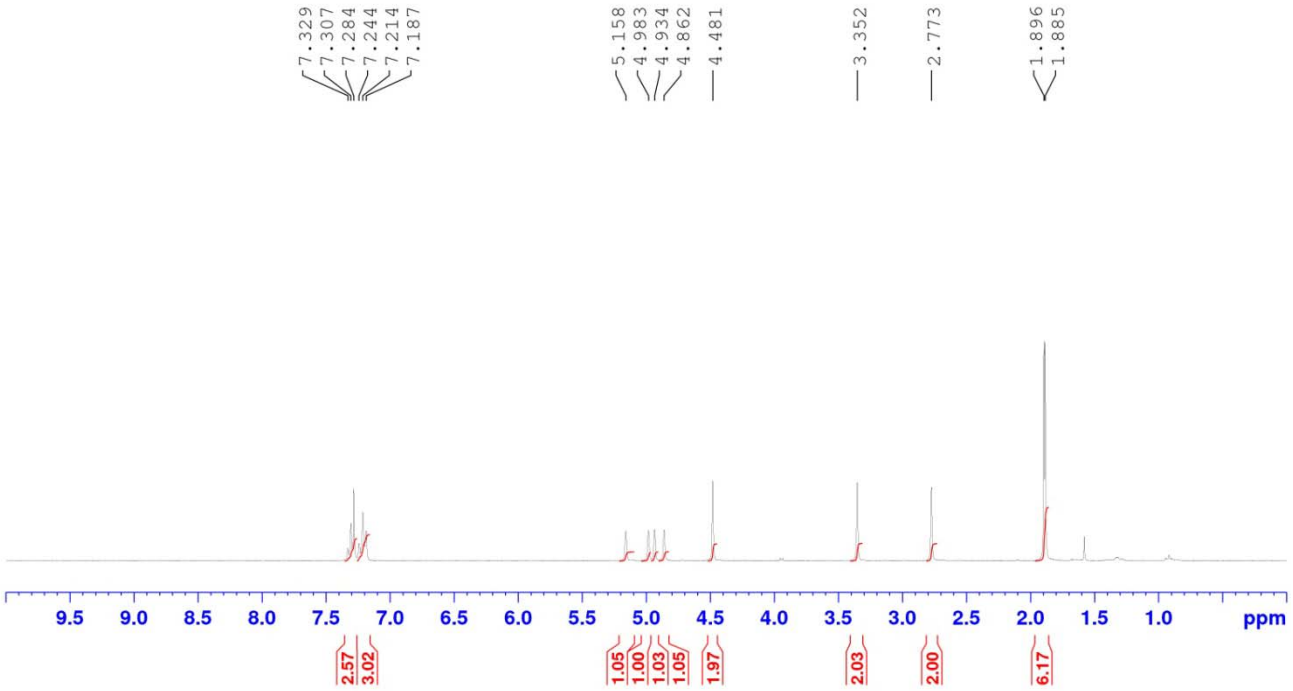
^{1}H NMR



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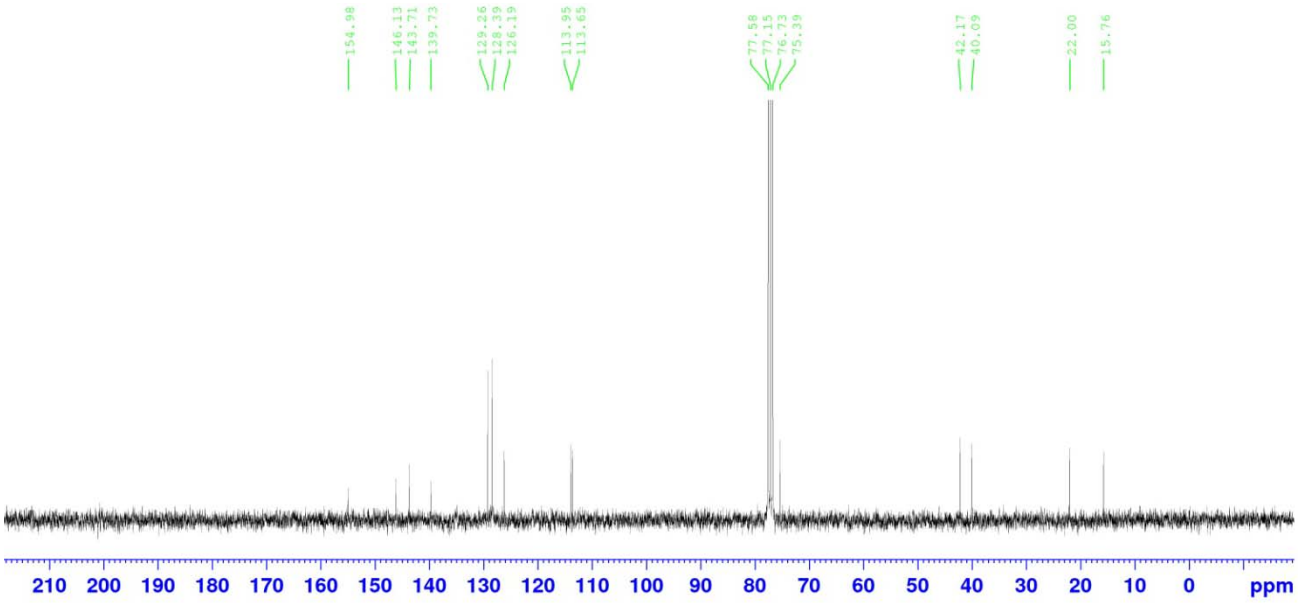
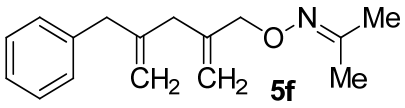


^{13}C DEPT 135 NMR



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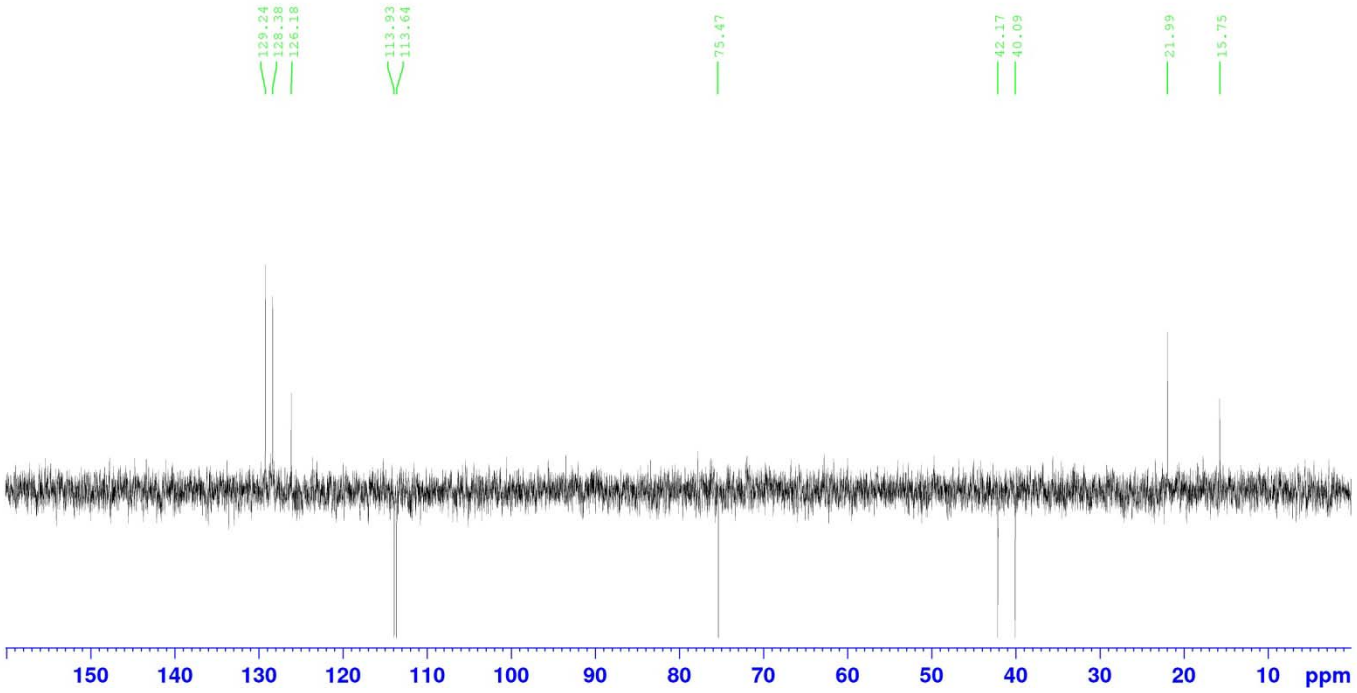
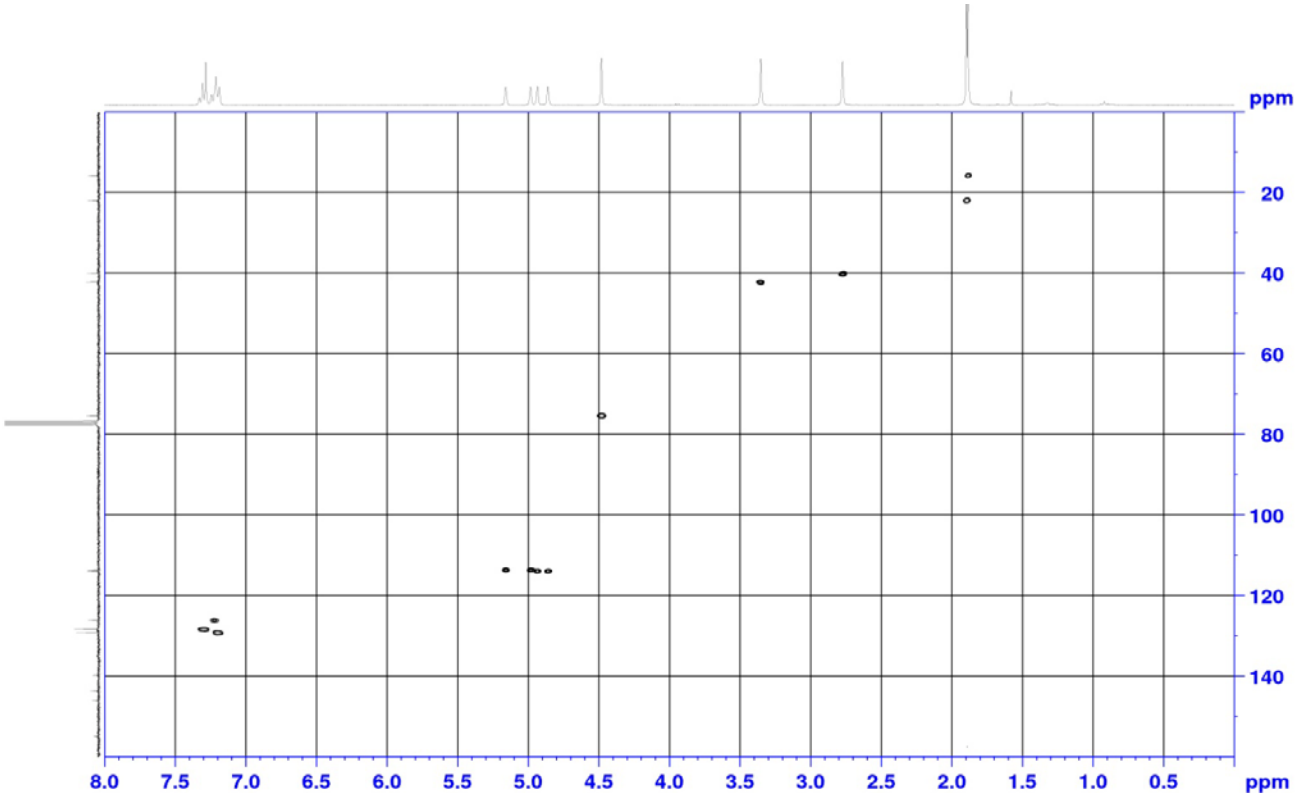
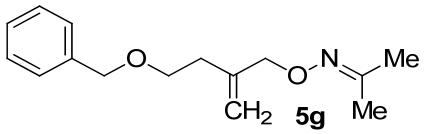
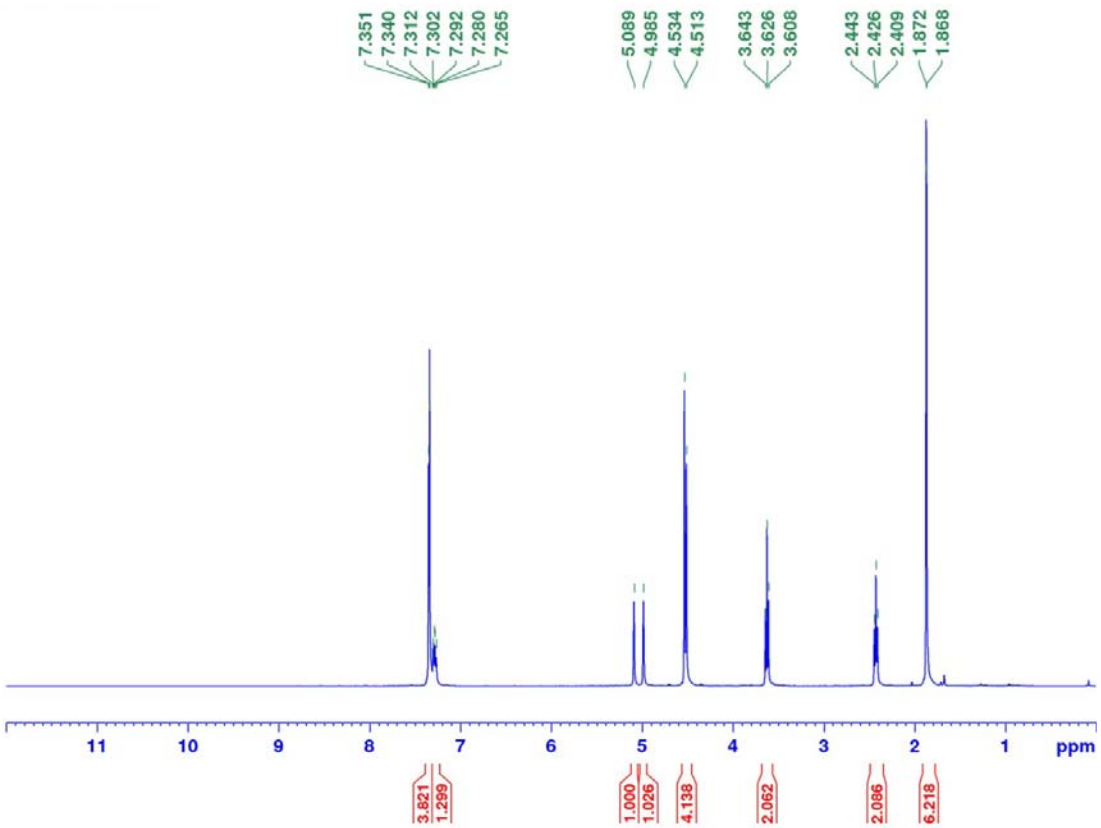


^{1}H- ^{13}C HSQC NMR

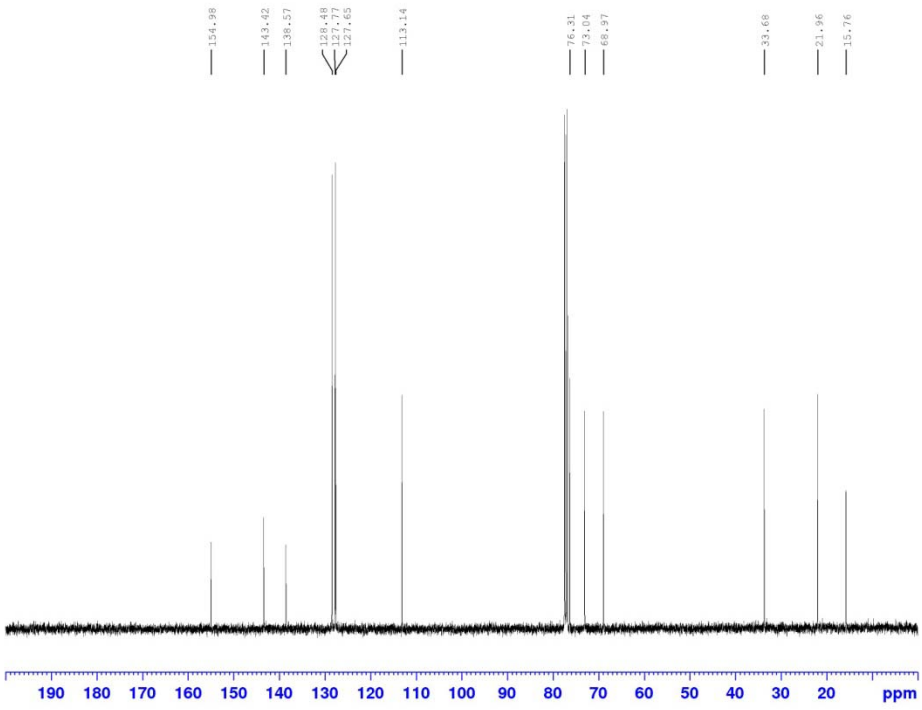


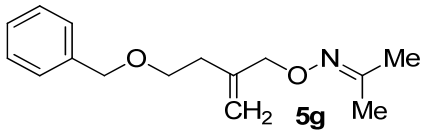


^{1}H NMR



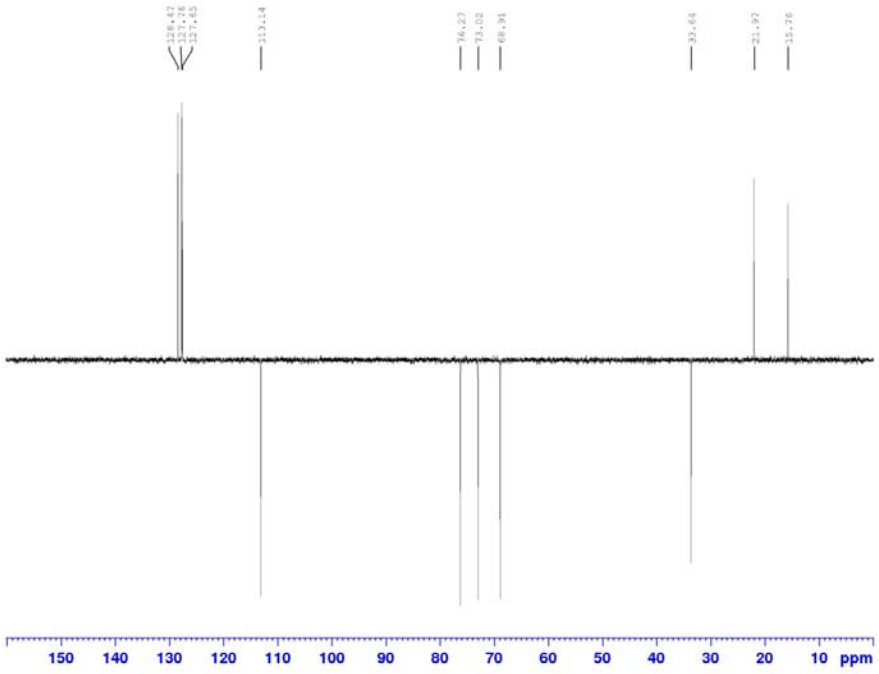
^{13}C NMR



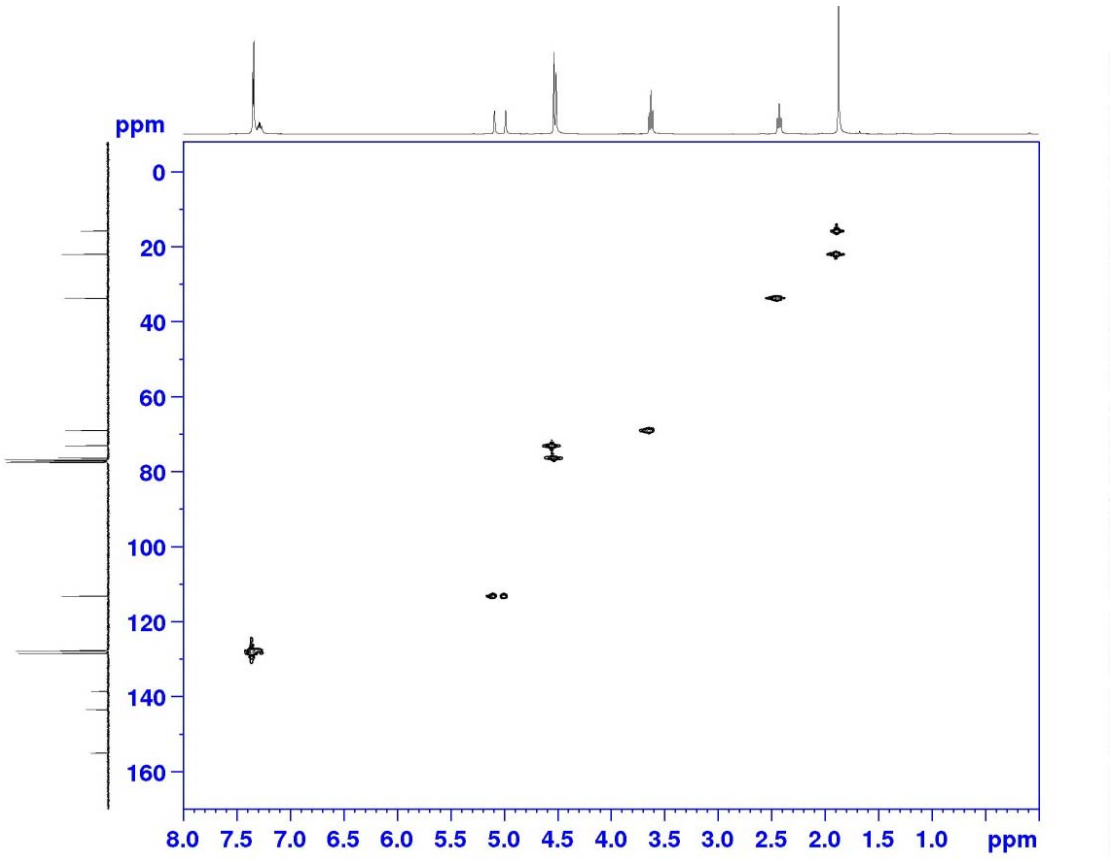


5g

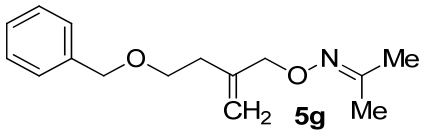
^{13}C DEPT135 NMR



^{1}H-^{13}C HSQC NMR



^{1}H-^{13}C HMBC NMR



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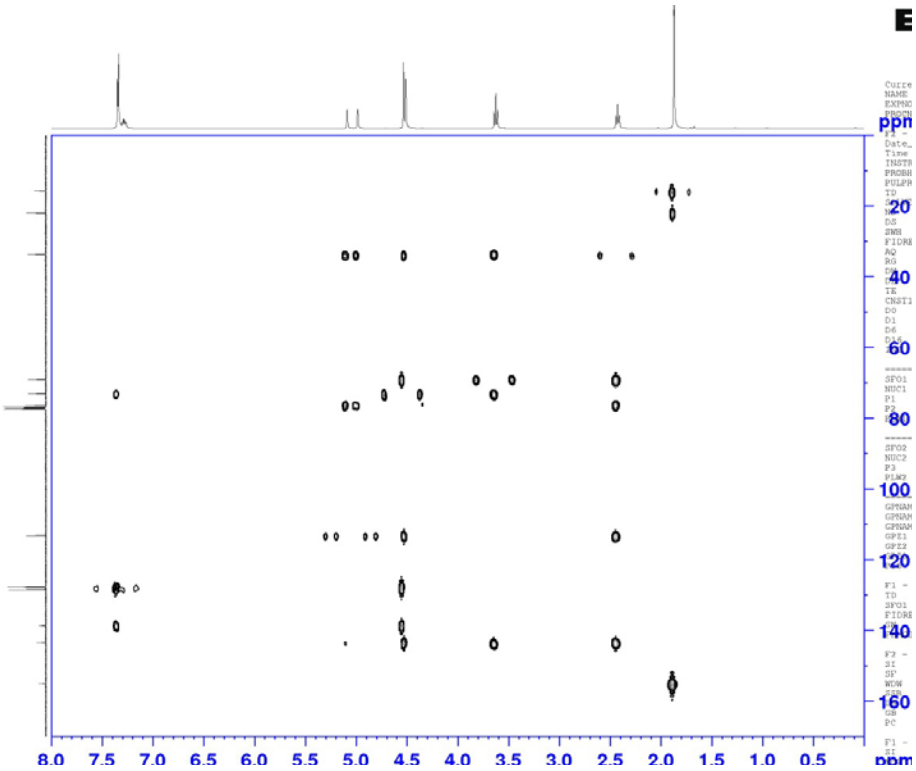

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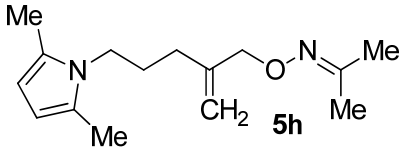

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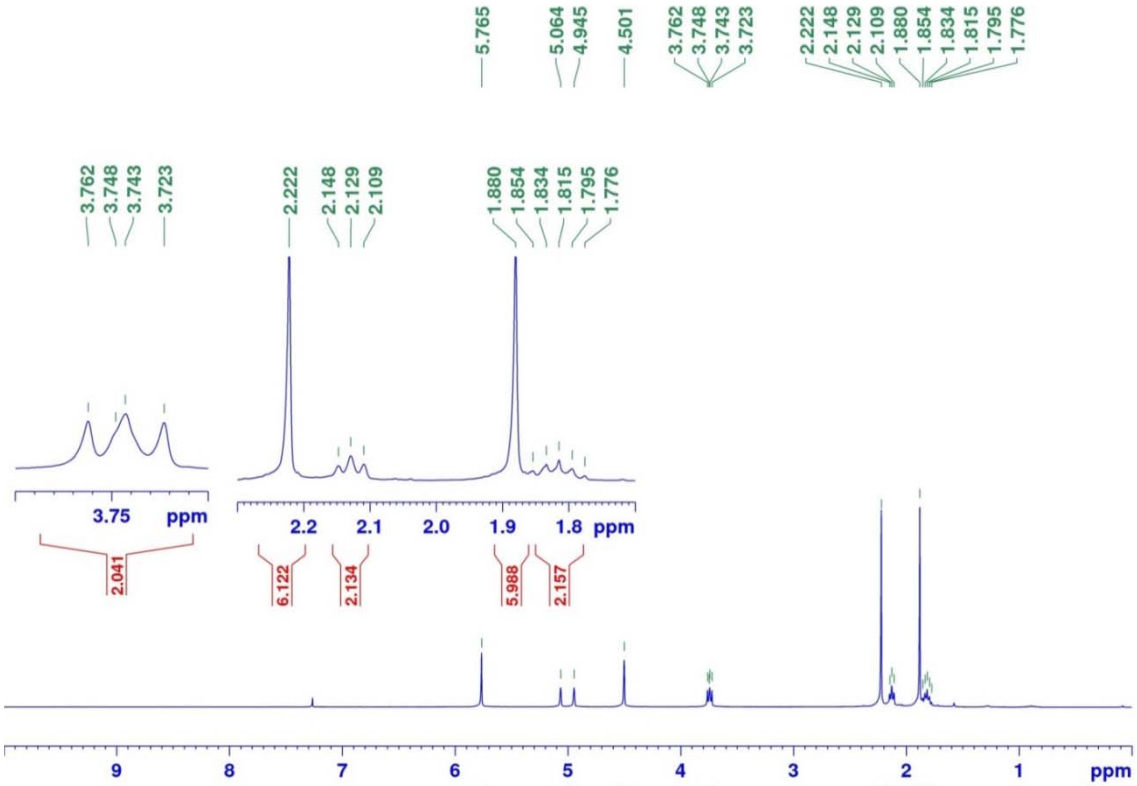

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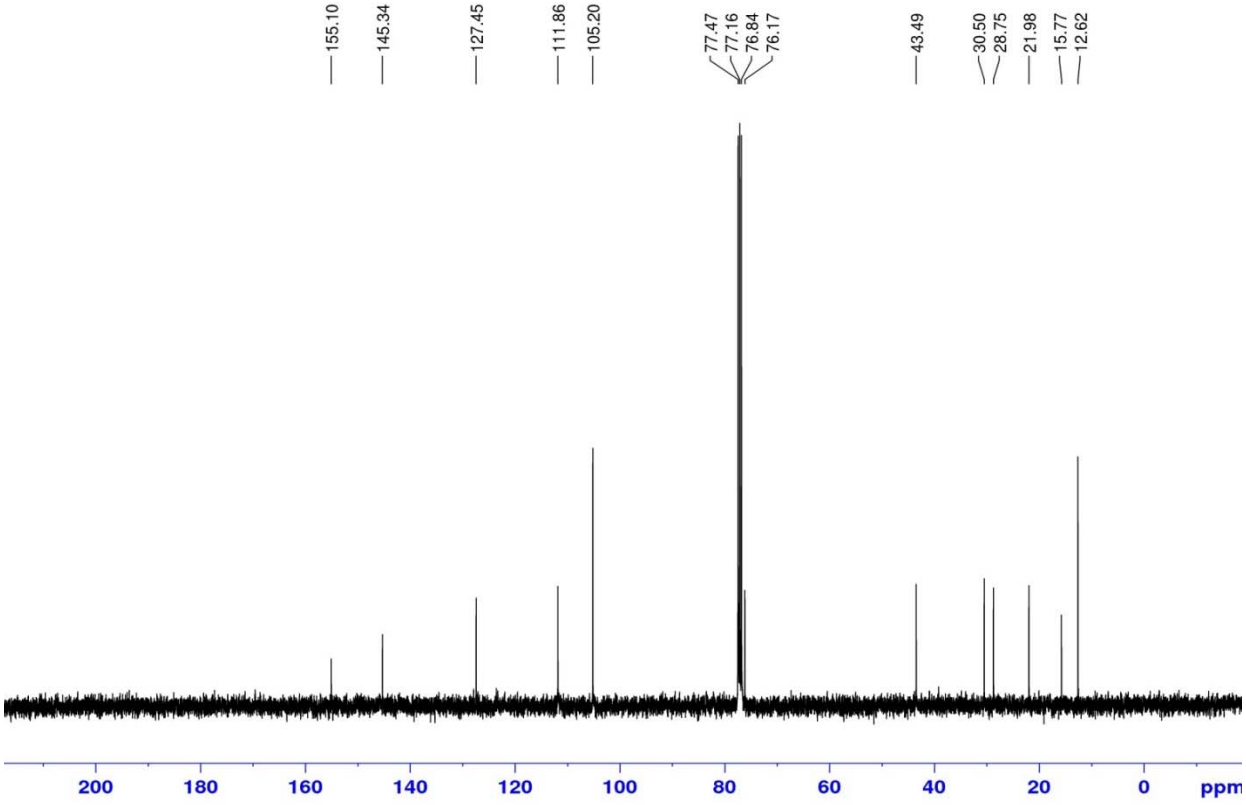

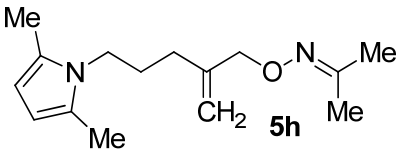

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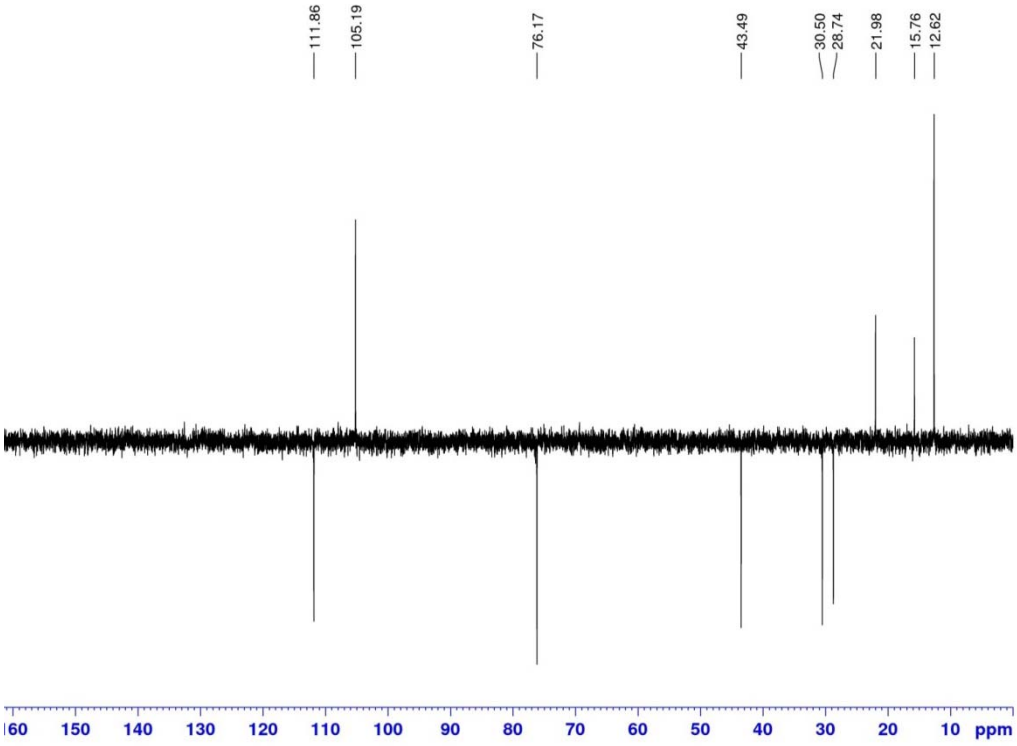
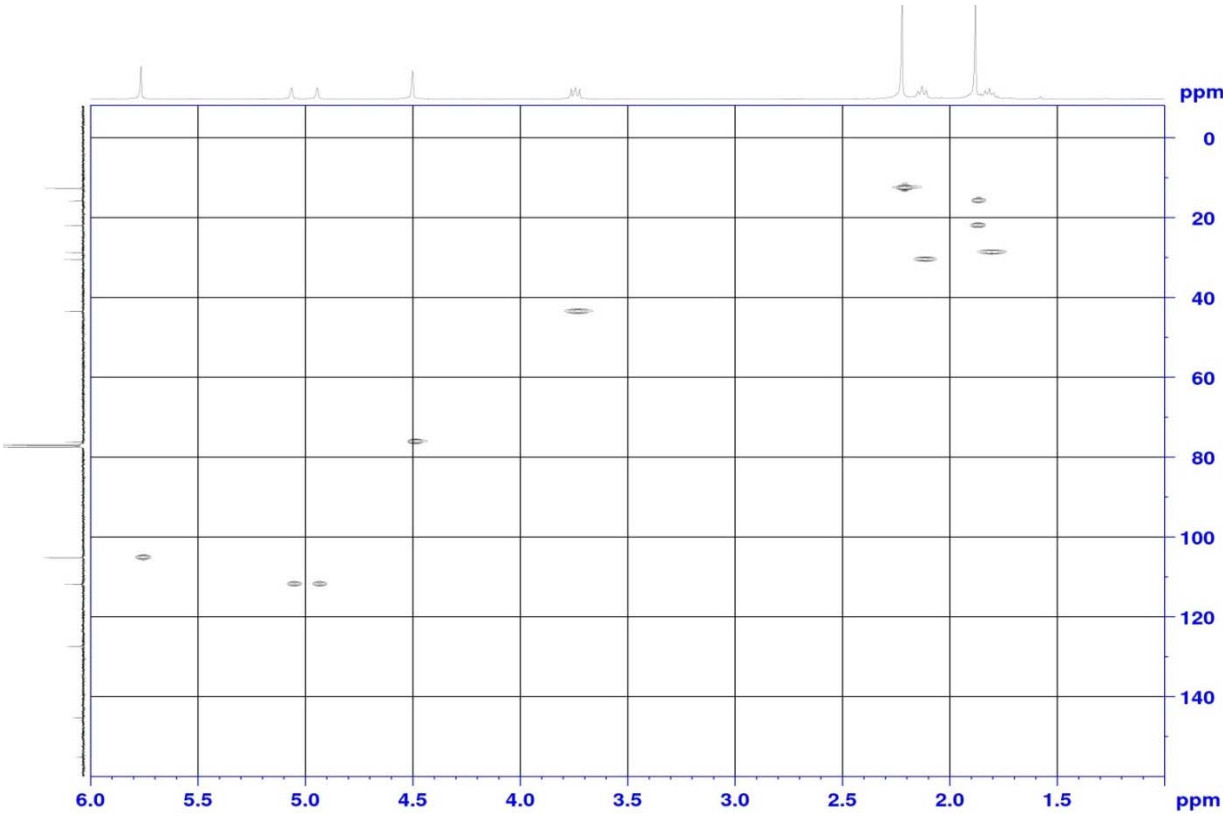
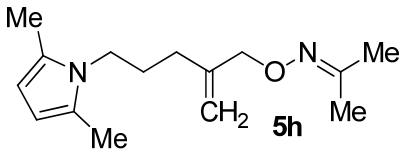
^{13}C DEPT 135 NMR



^{1}H- ^{13}C HSQC NMR



^{1}H- ^{13}C HMBC NMR



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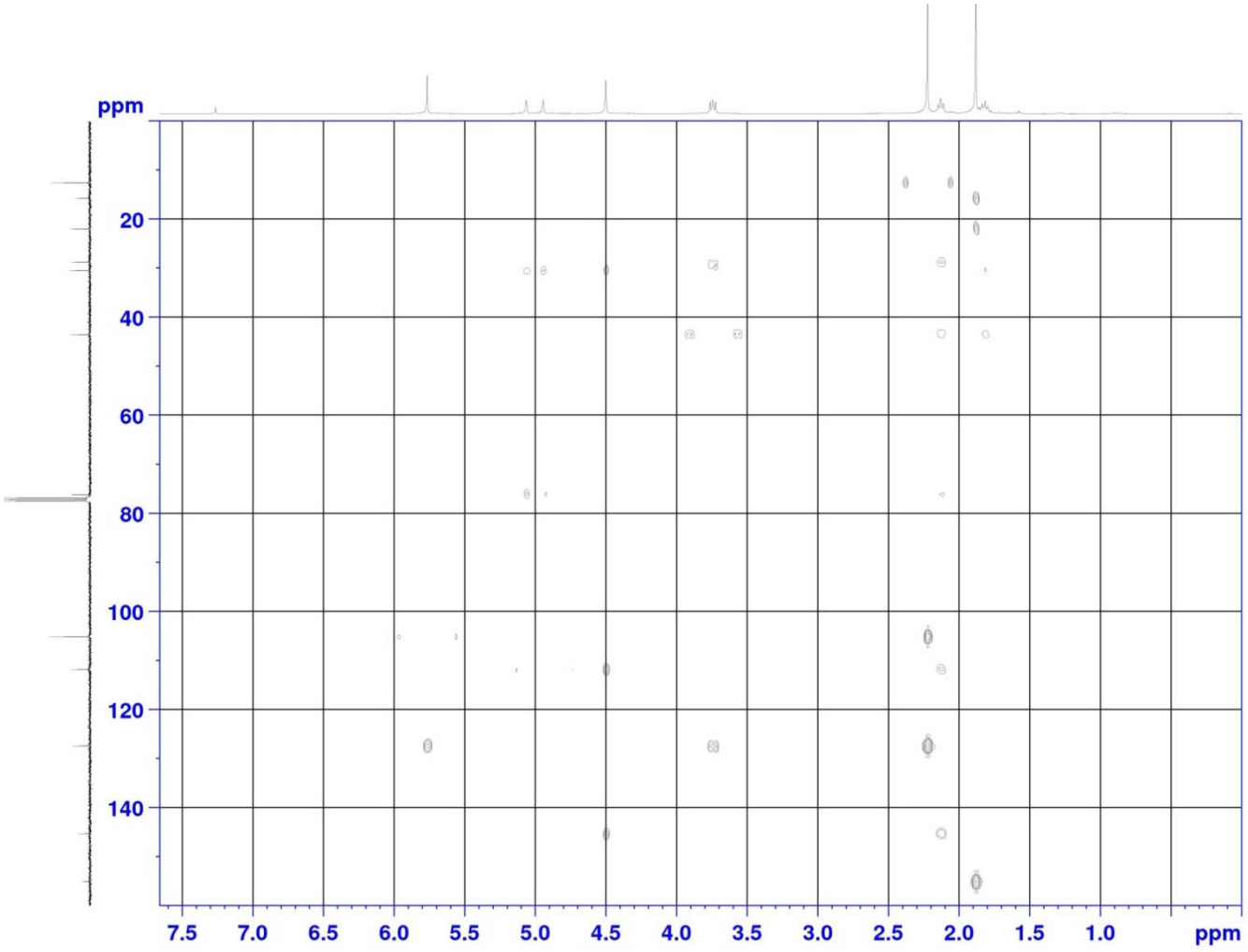

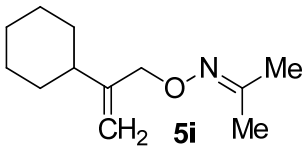

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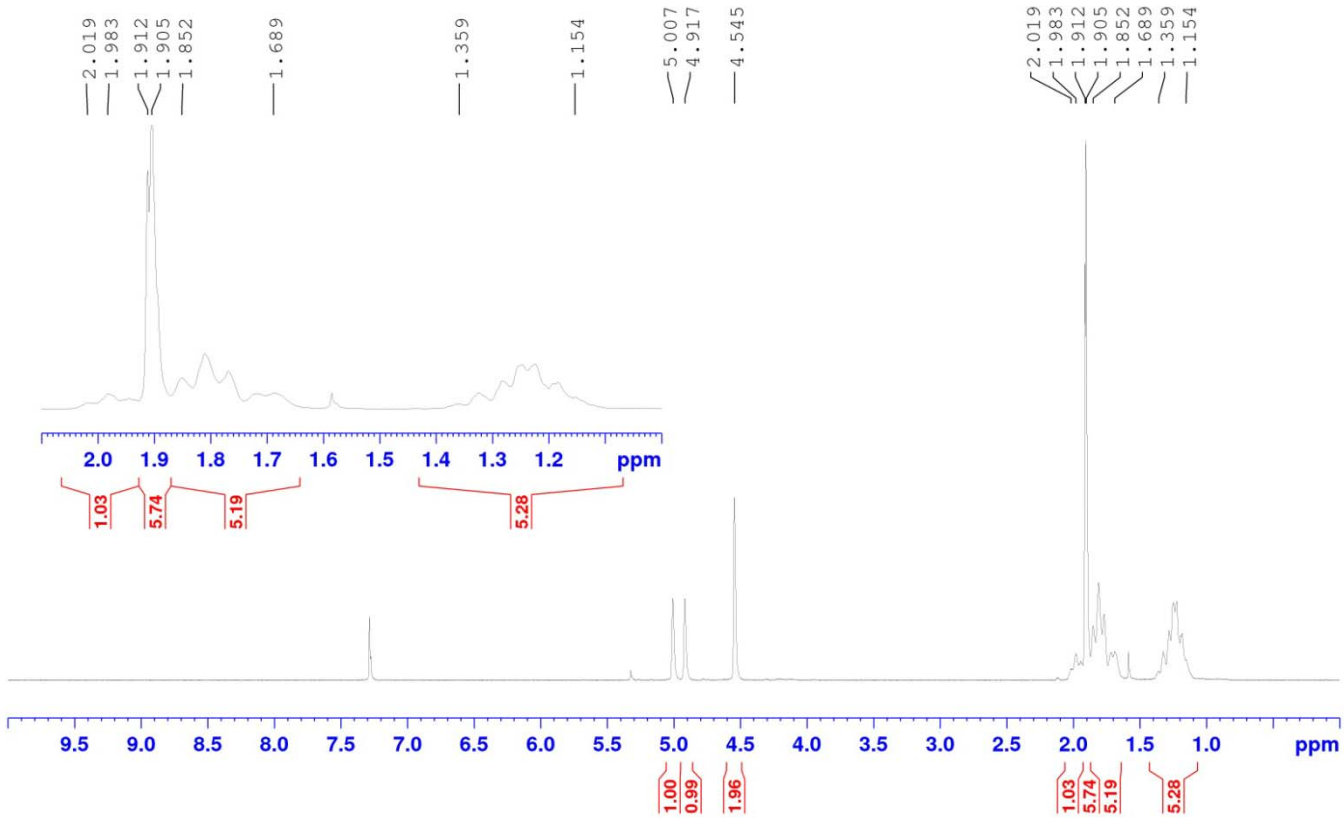

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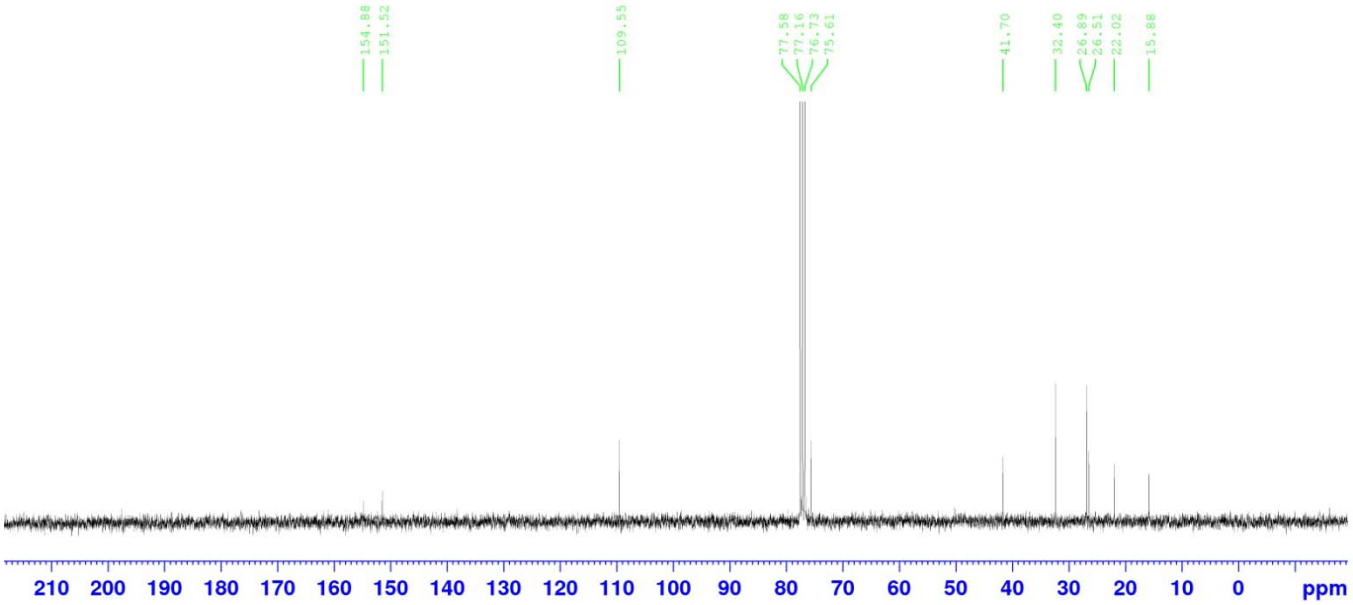
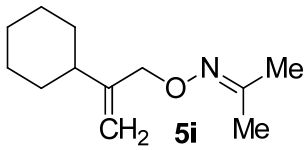
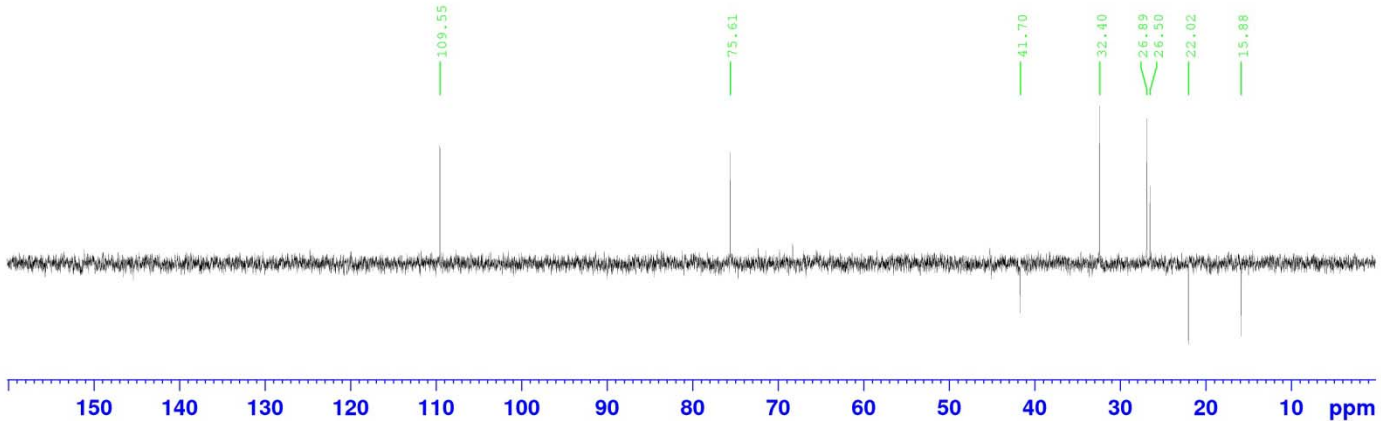


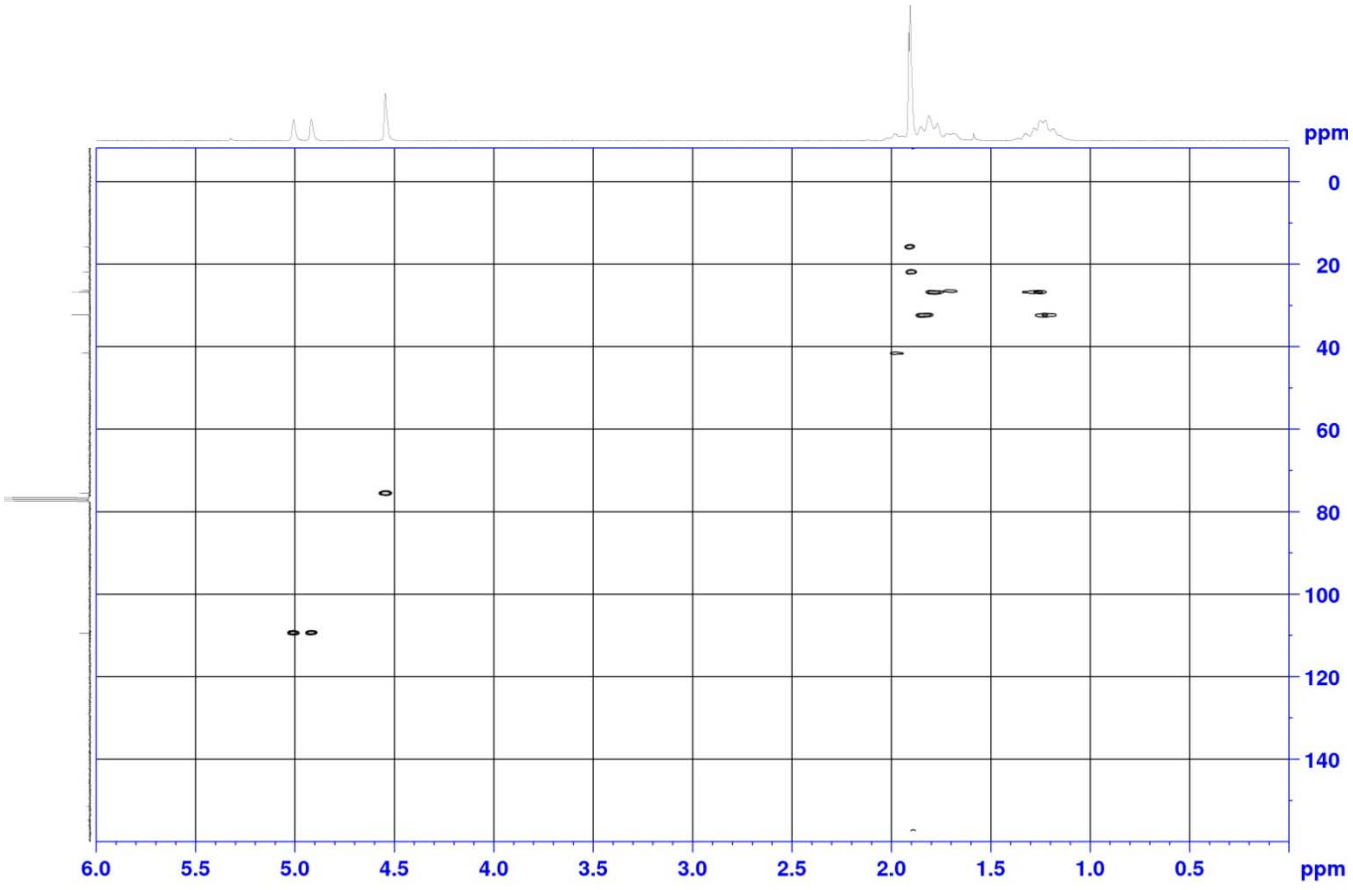


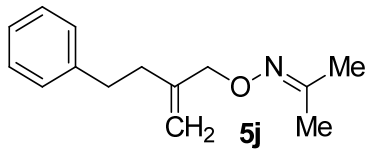
5i

^{13}C DEPT 135 NMR



^{1}H-^{13}C HSQC NMR





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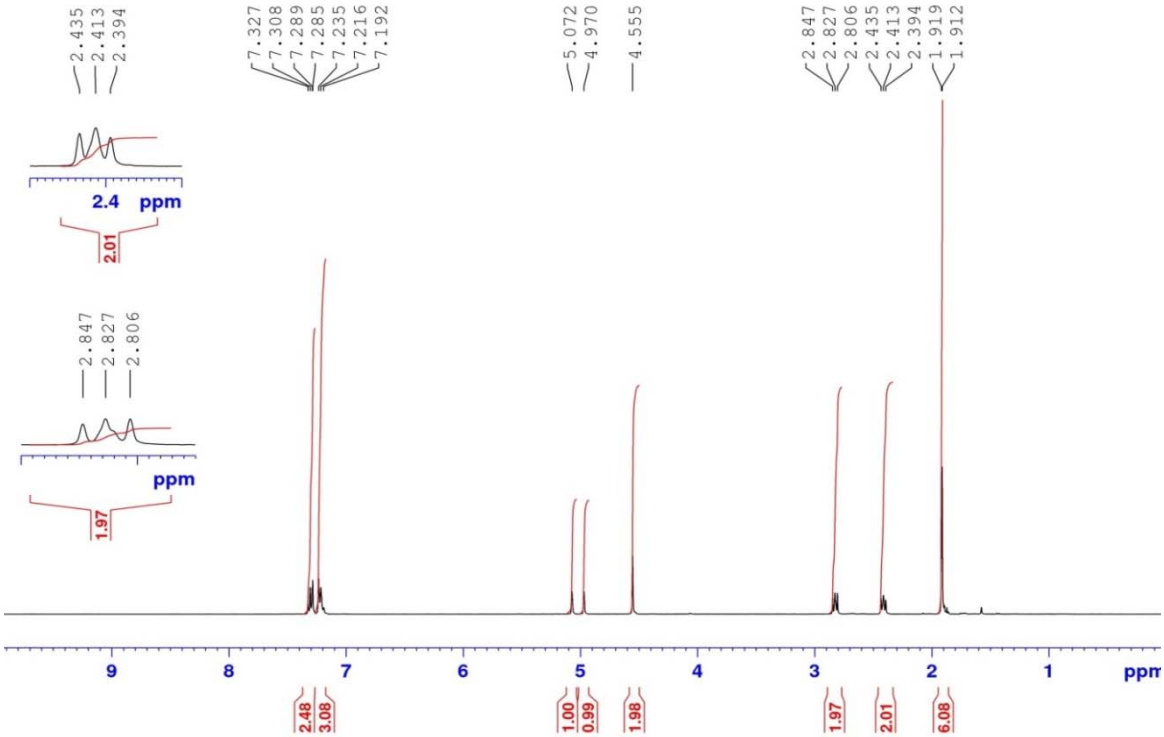

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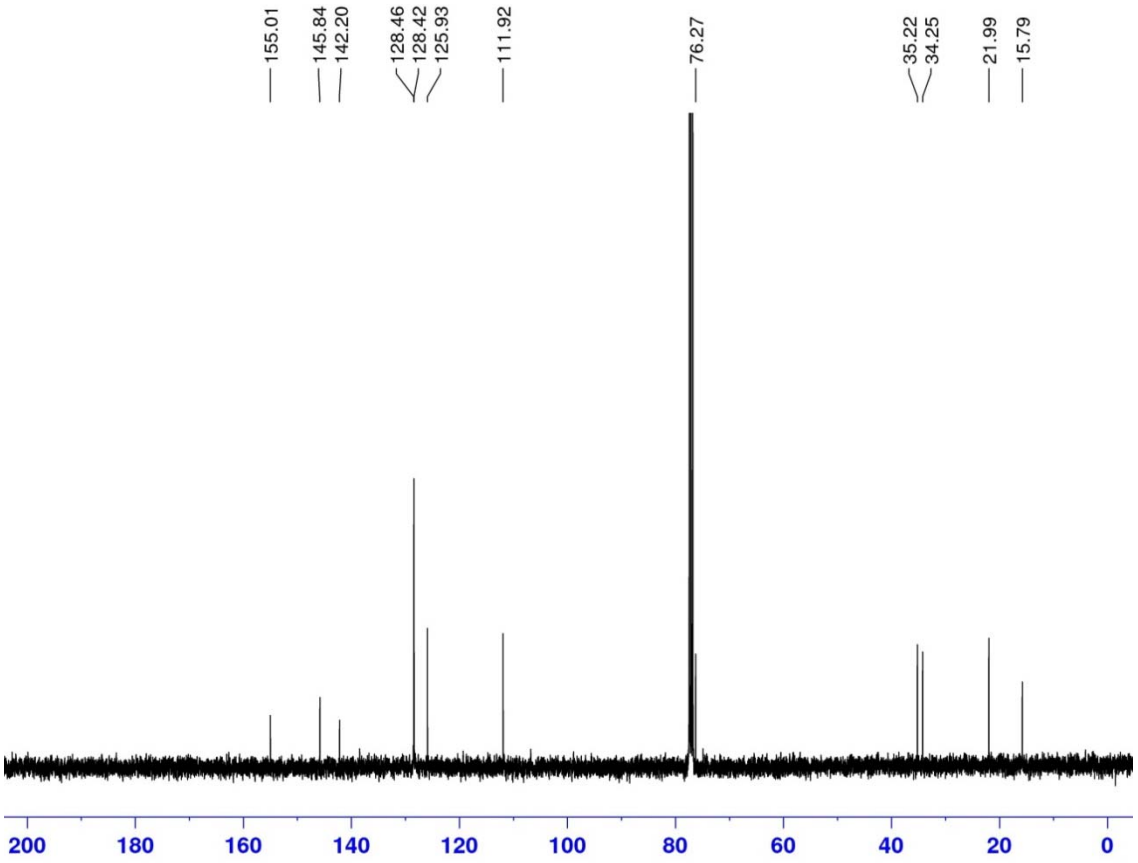

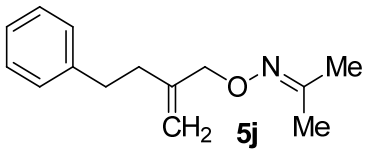

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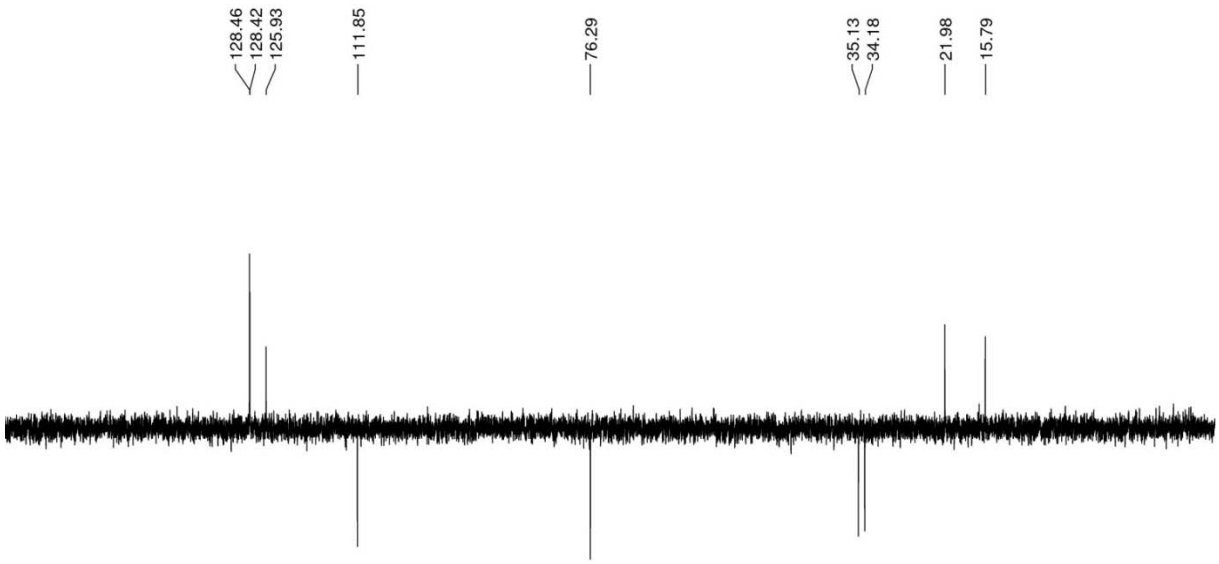

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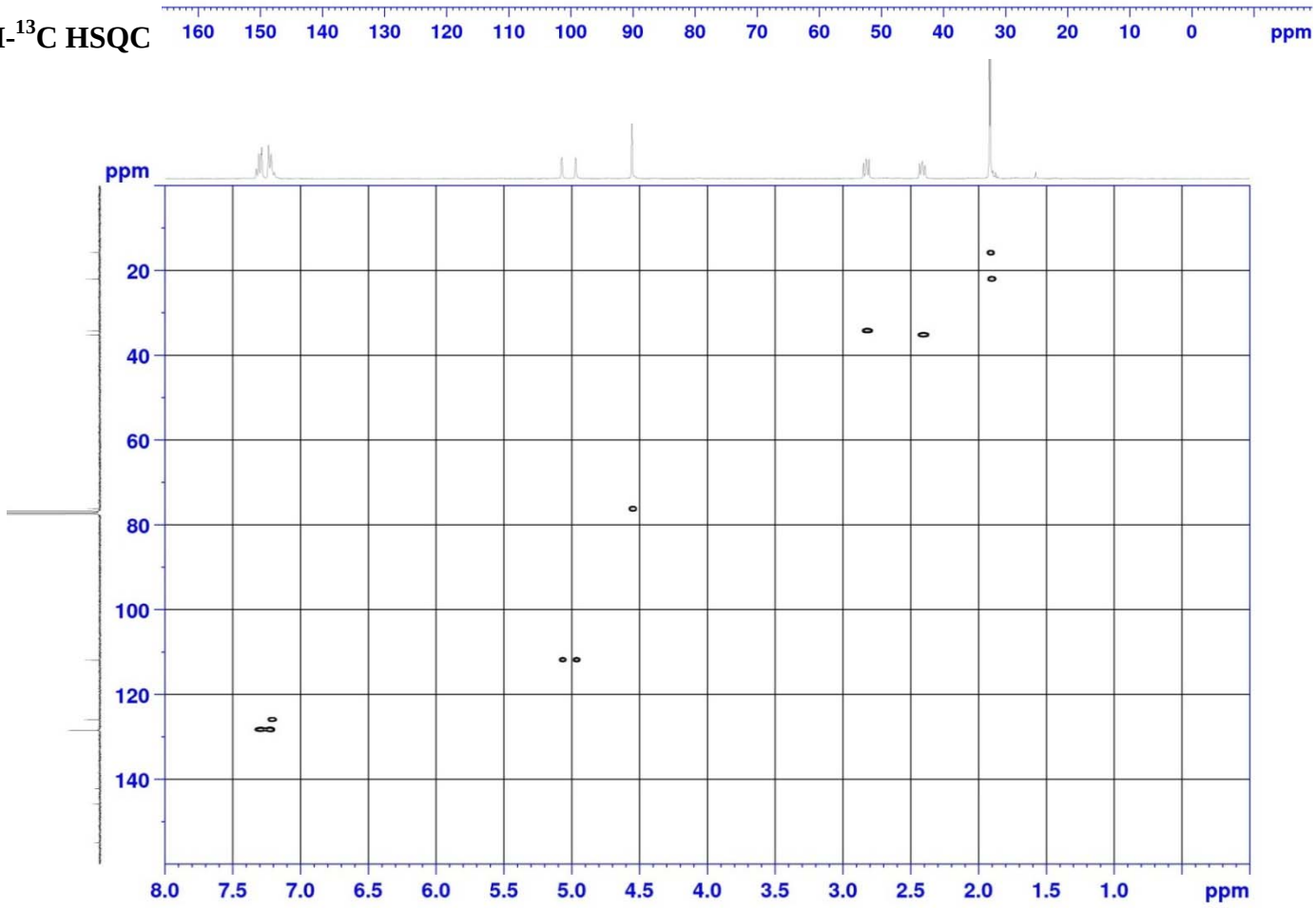
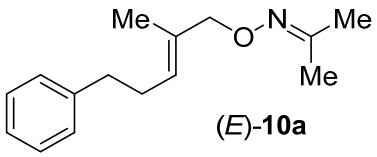
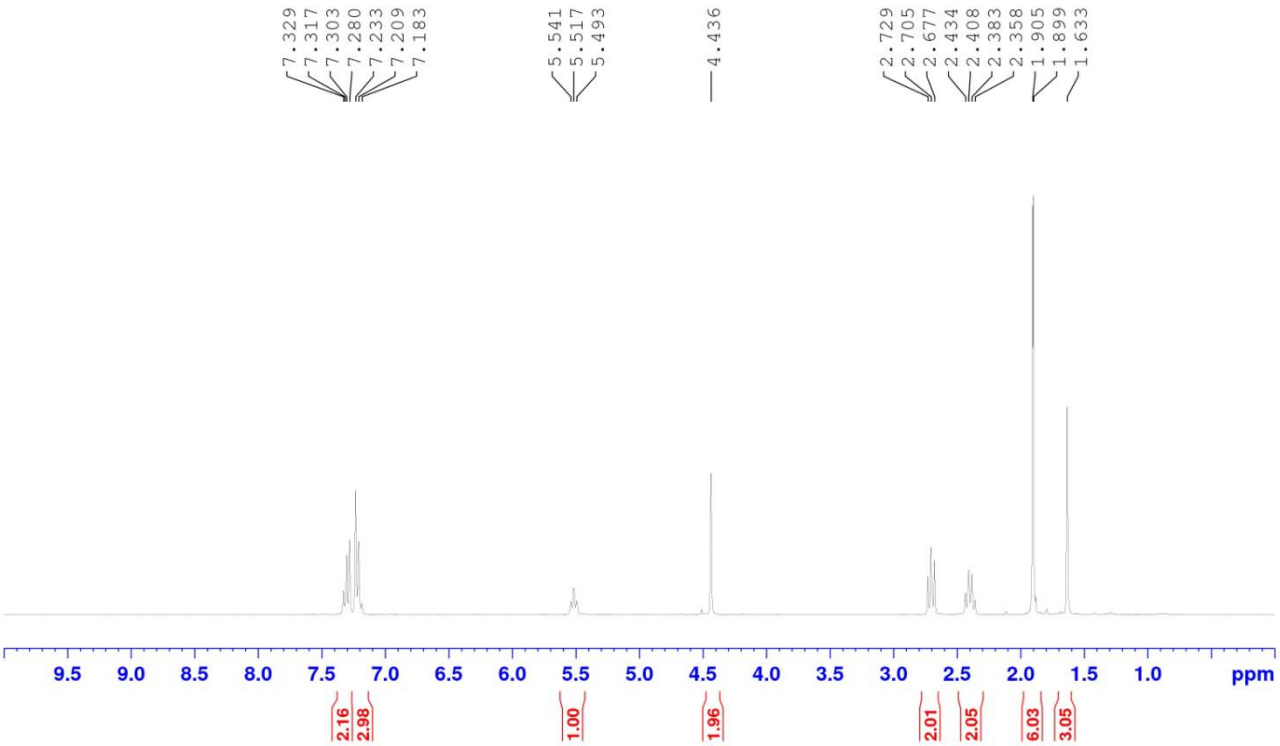




(*E*)-**10a**

^{1}H NMR



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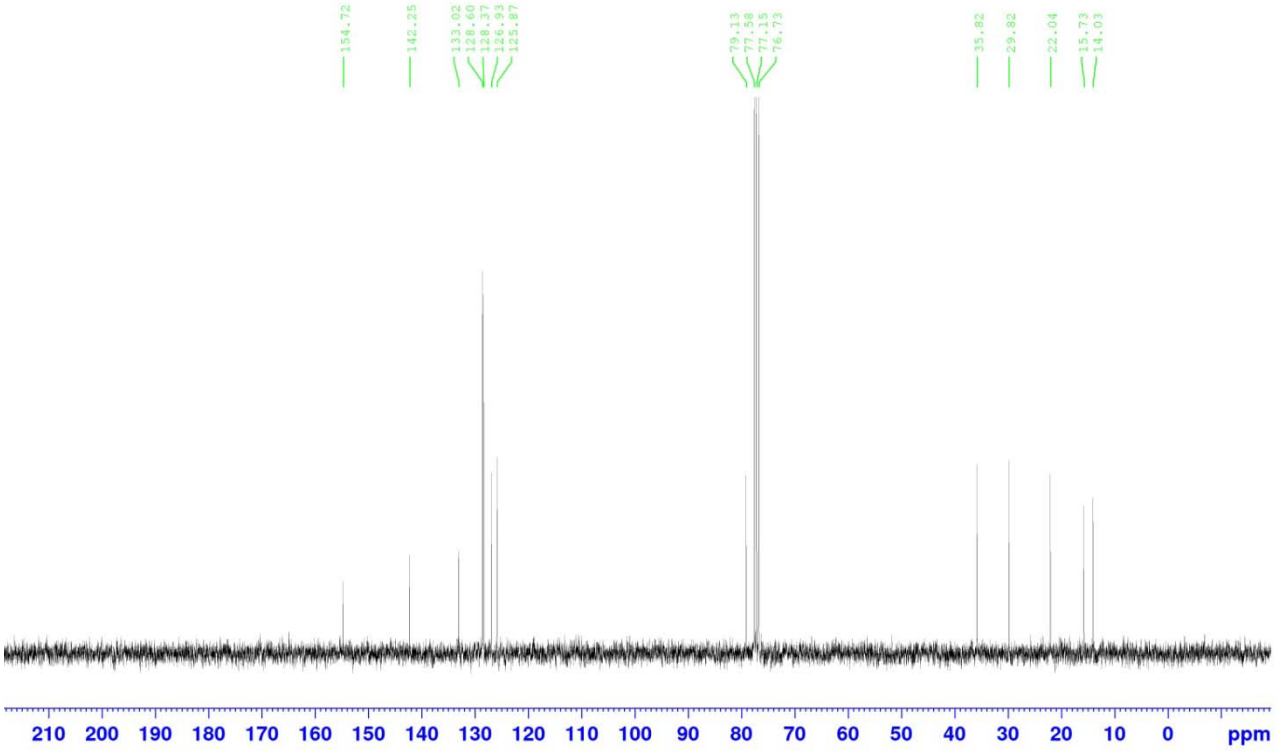
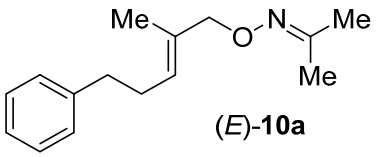
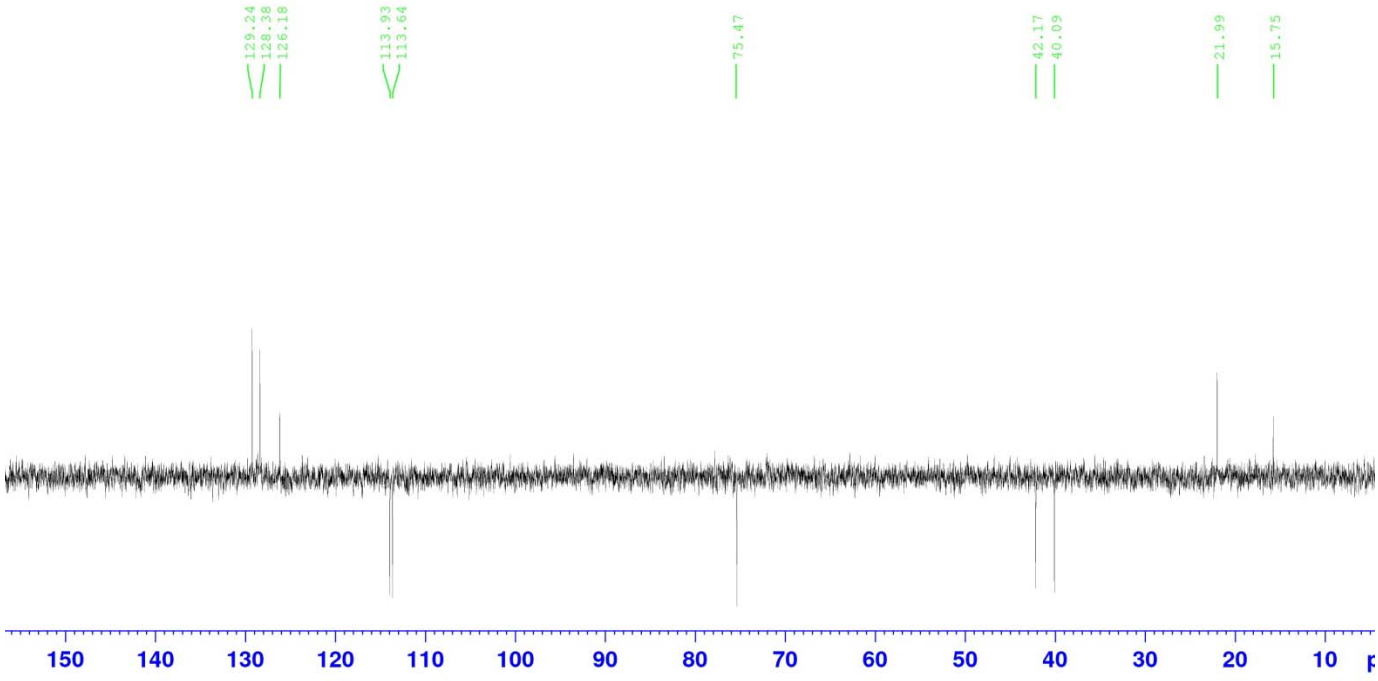


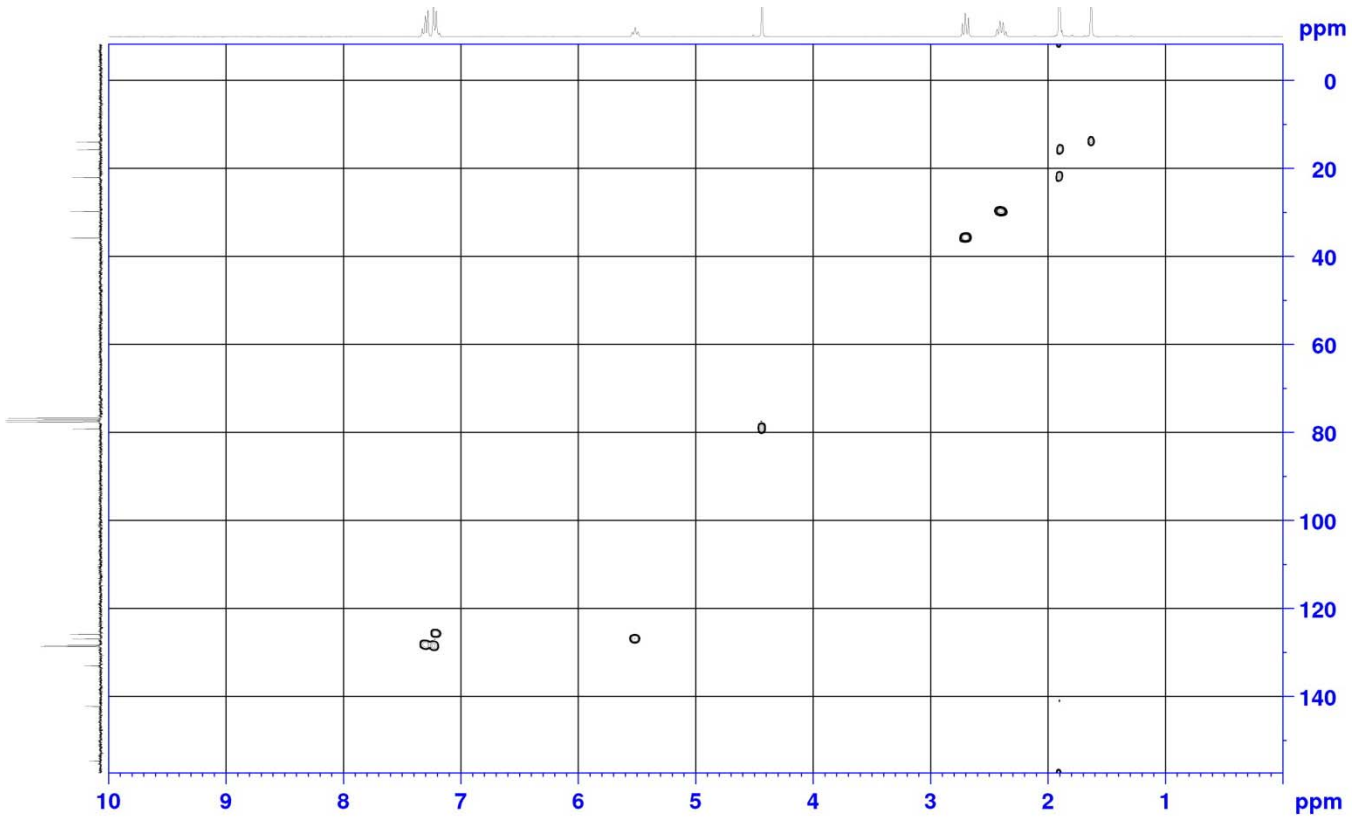


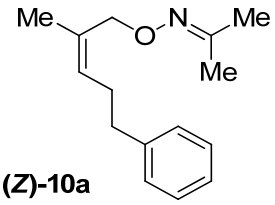
(*E*)-**10a**

^{13}C DEPT NMR



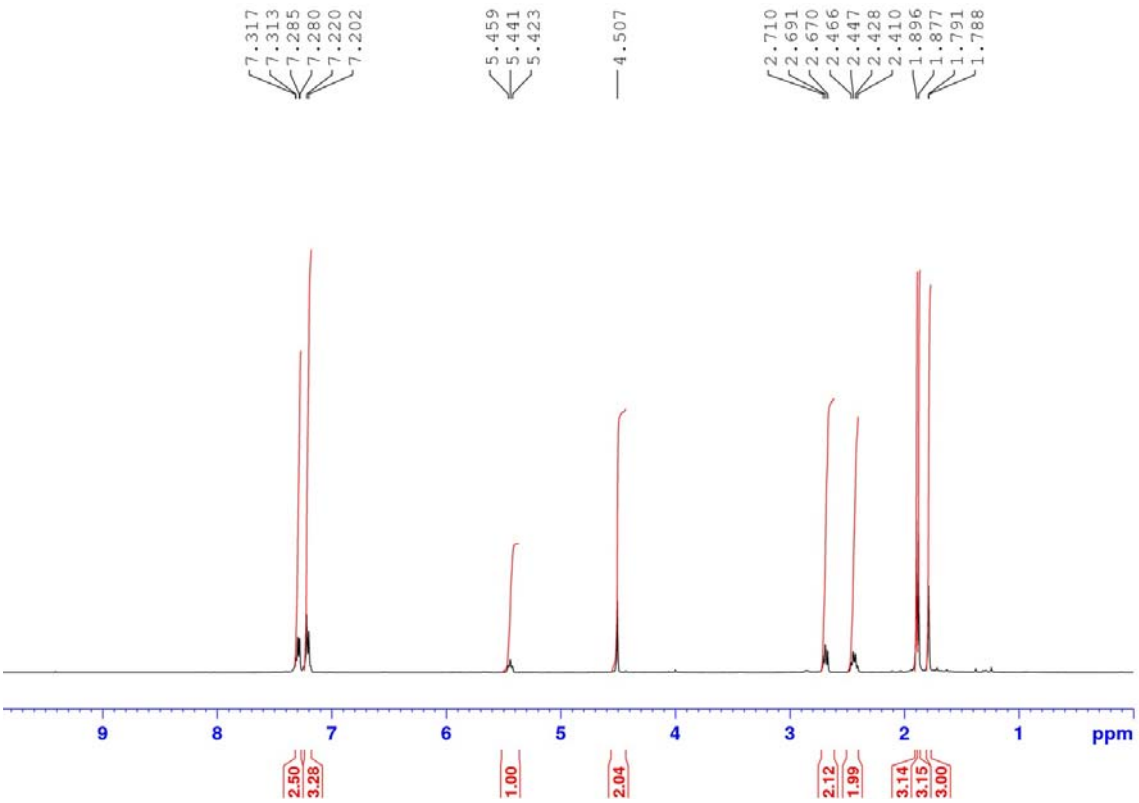
^{1}H- ^{13}C HSQC NMR





(*Z*)-10a

^{1}H NMR



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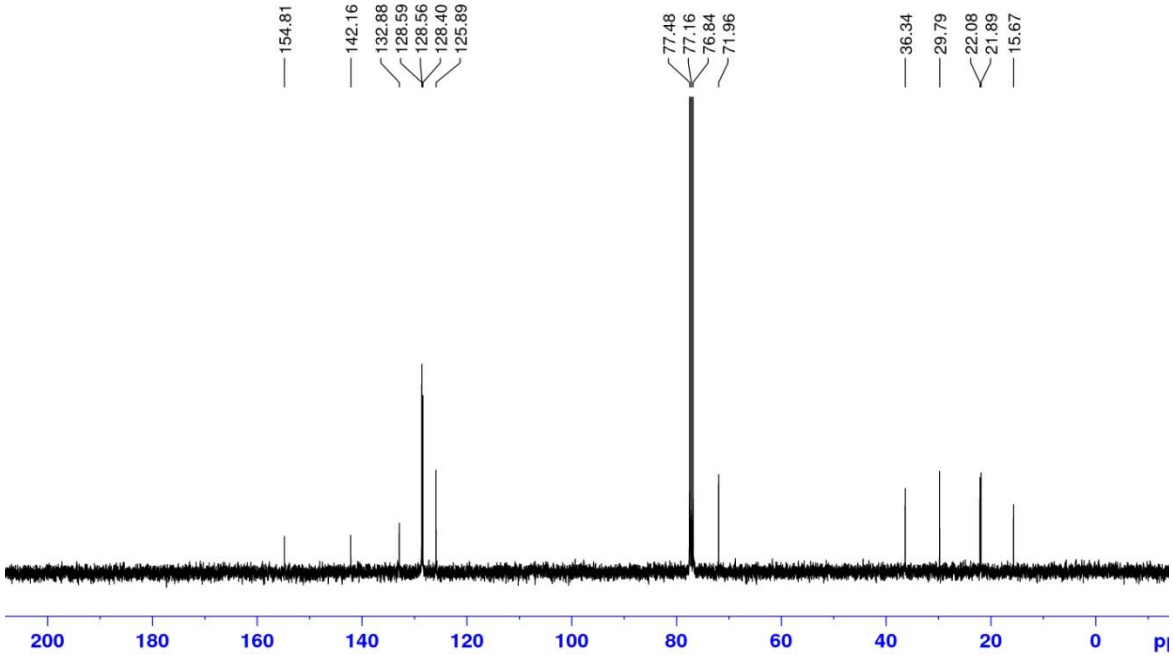
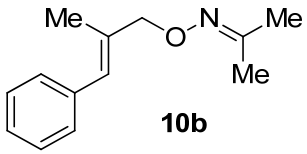
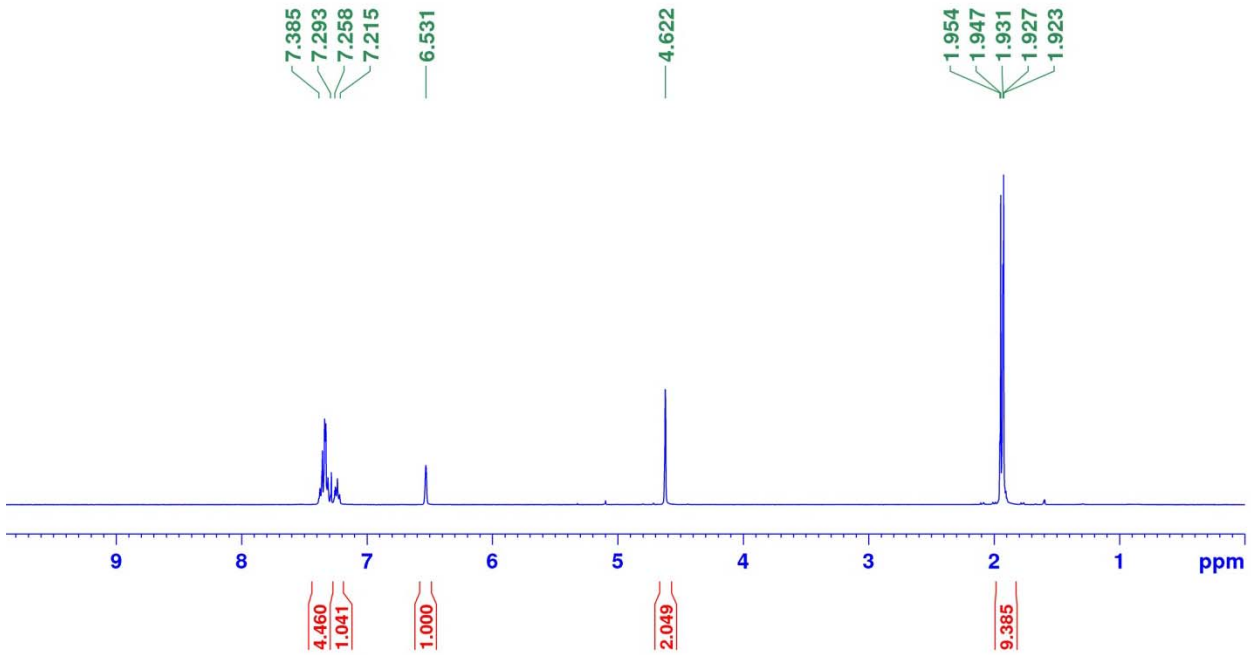


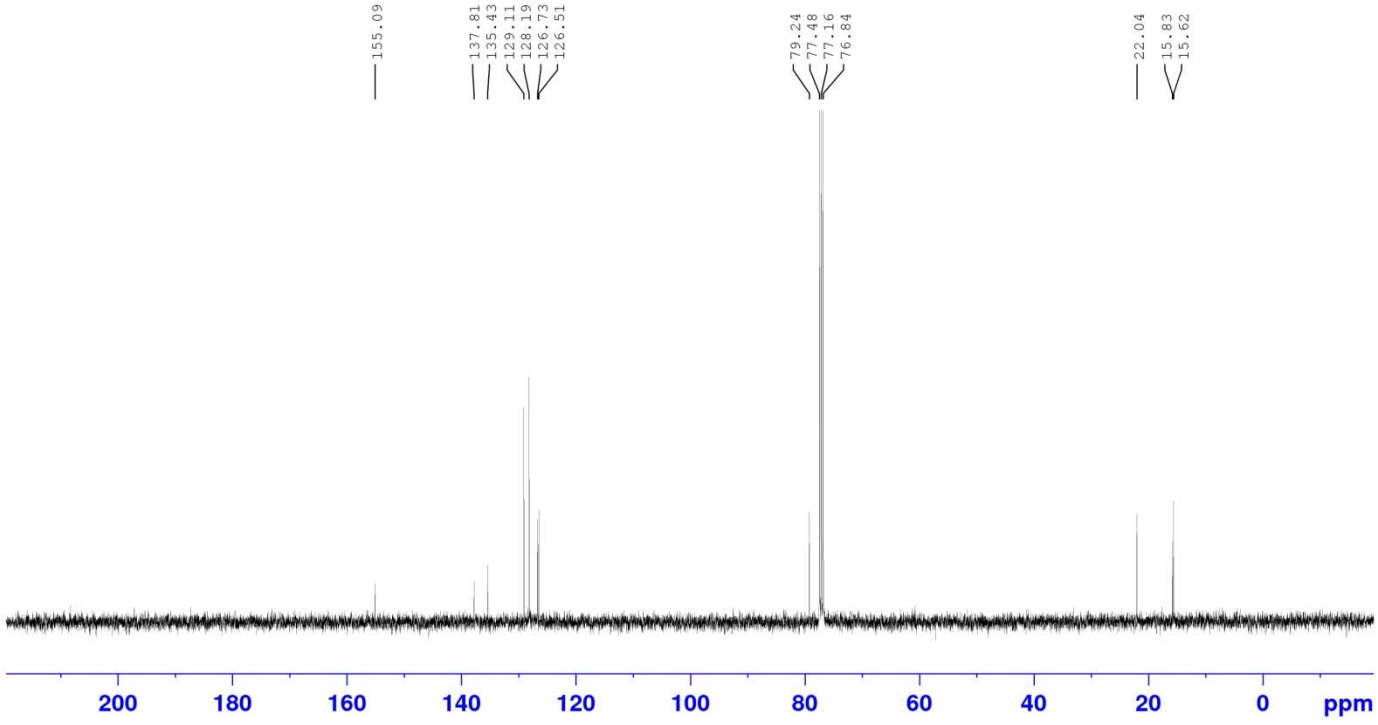


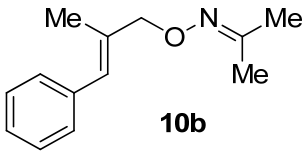
10b

^{1}H NMR



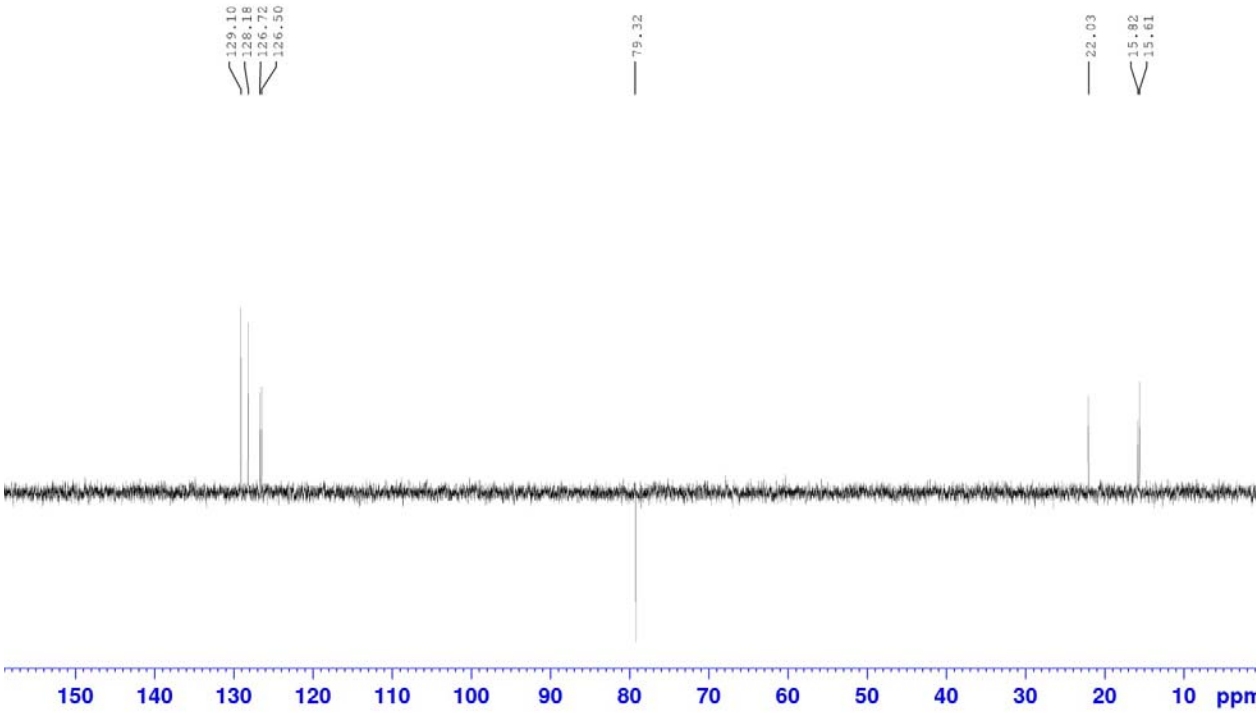
^{13}C NMR



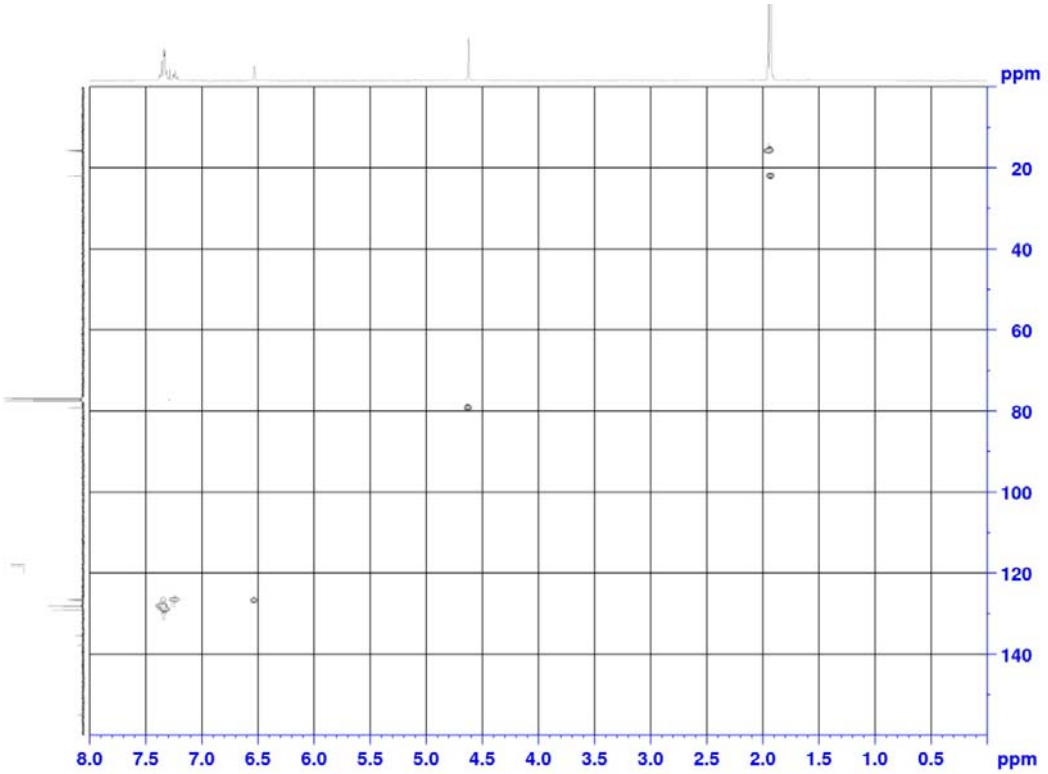


10b

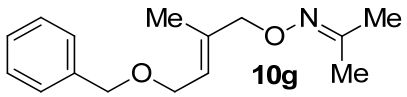
^{13}C DEPT NMR

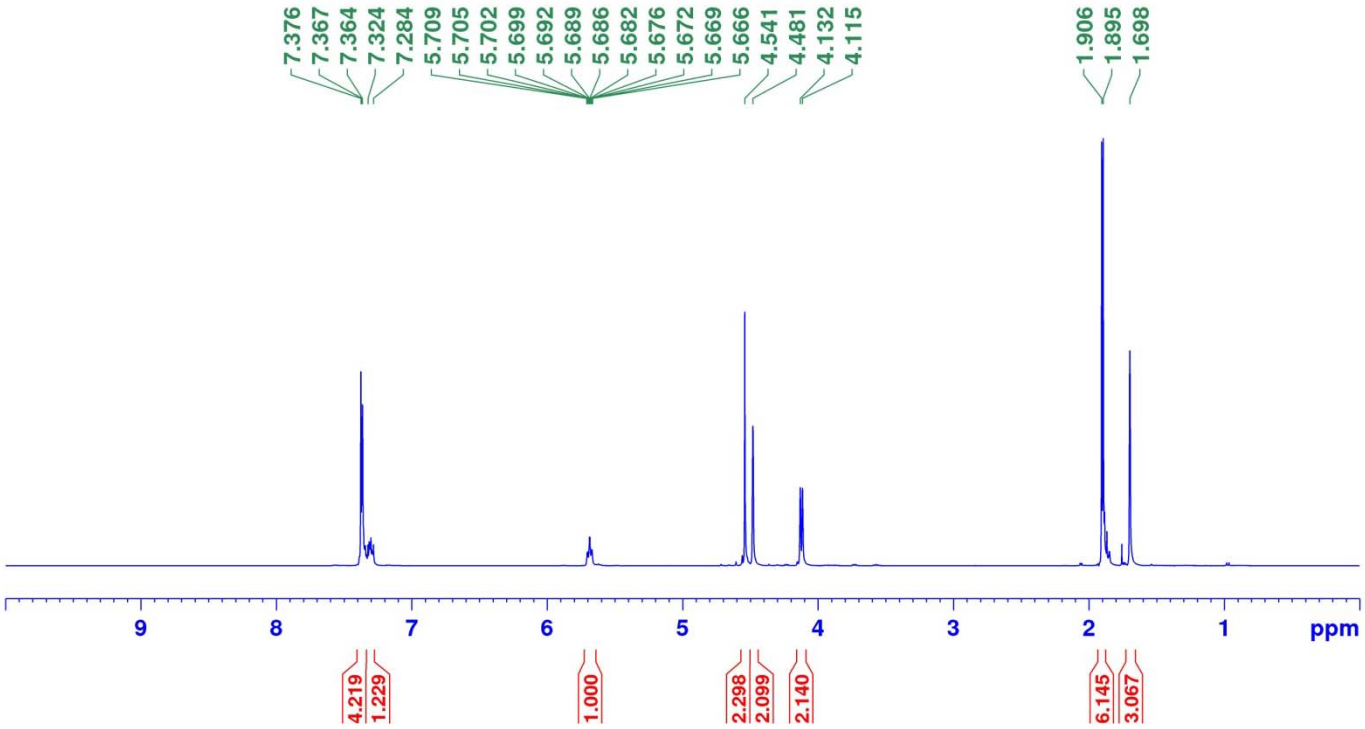


^{1}H-^{13}C HSQC NMR

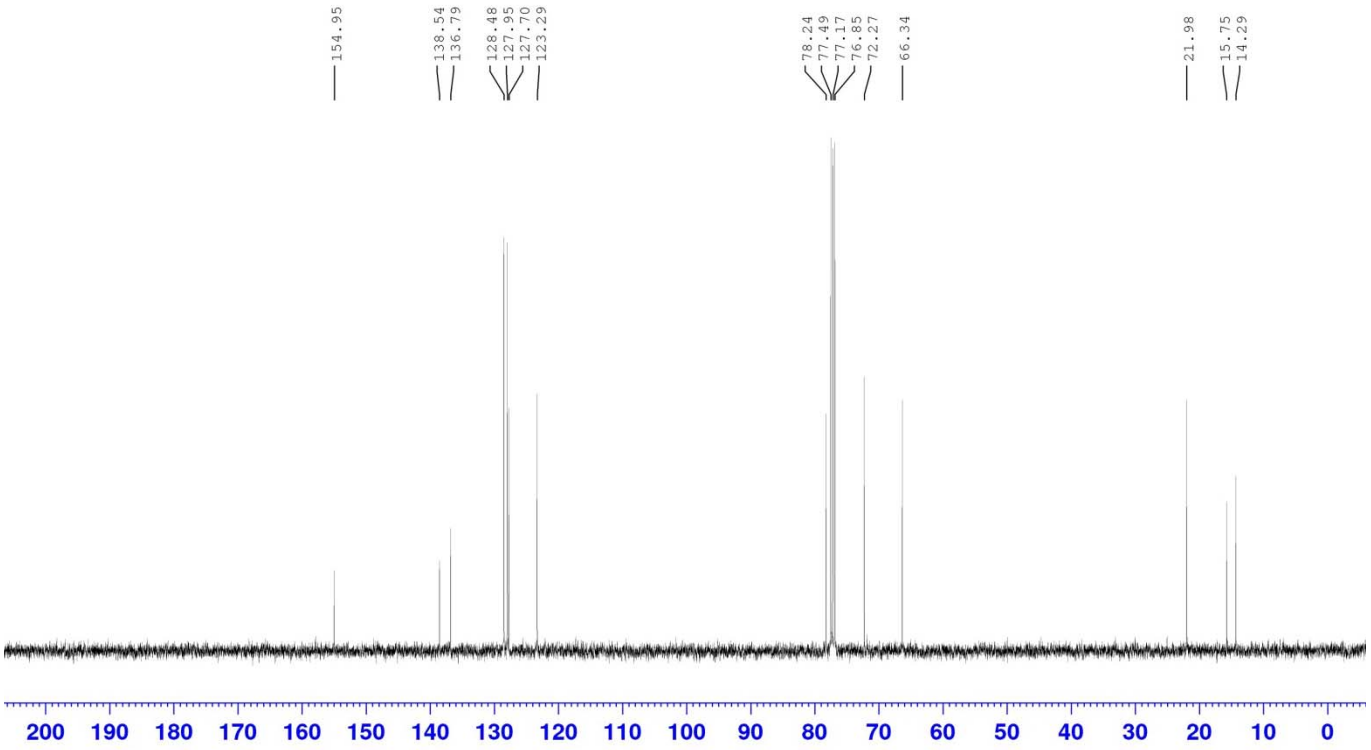


^{1}H NMR

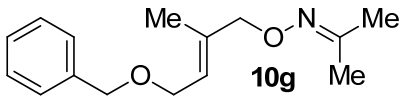


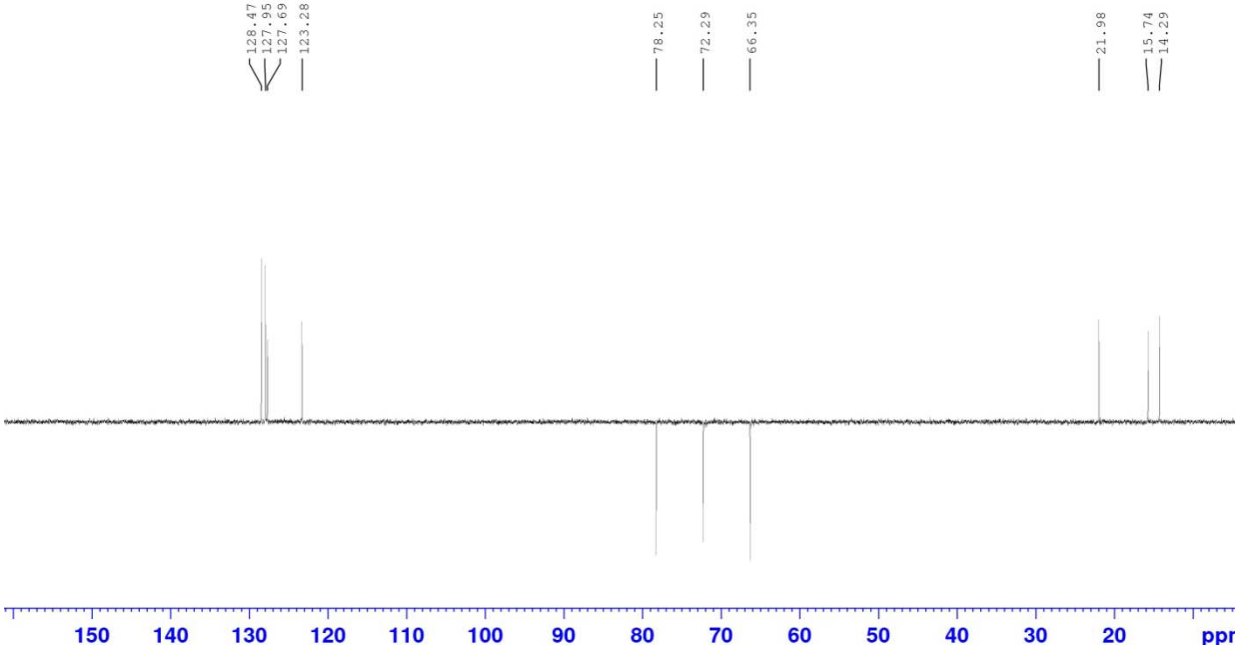


^{13}C NMR



^{13}C DEPT 135 NMR





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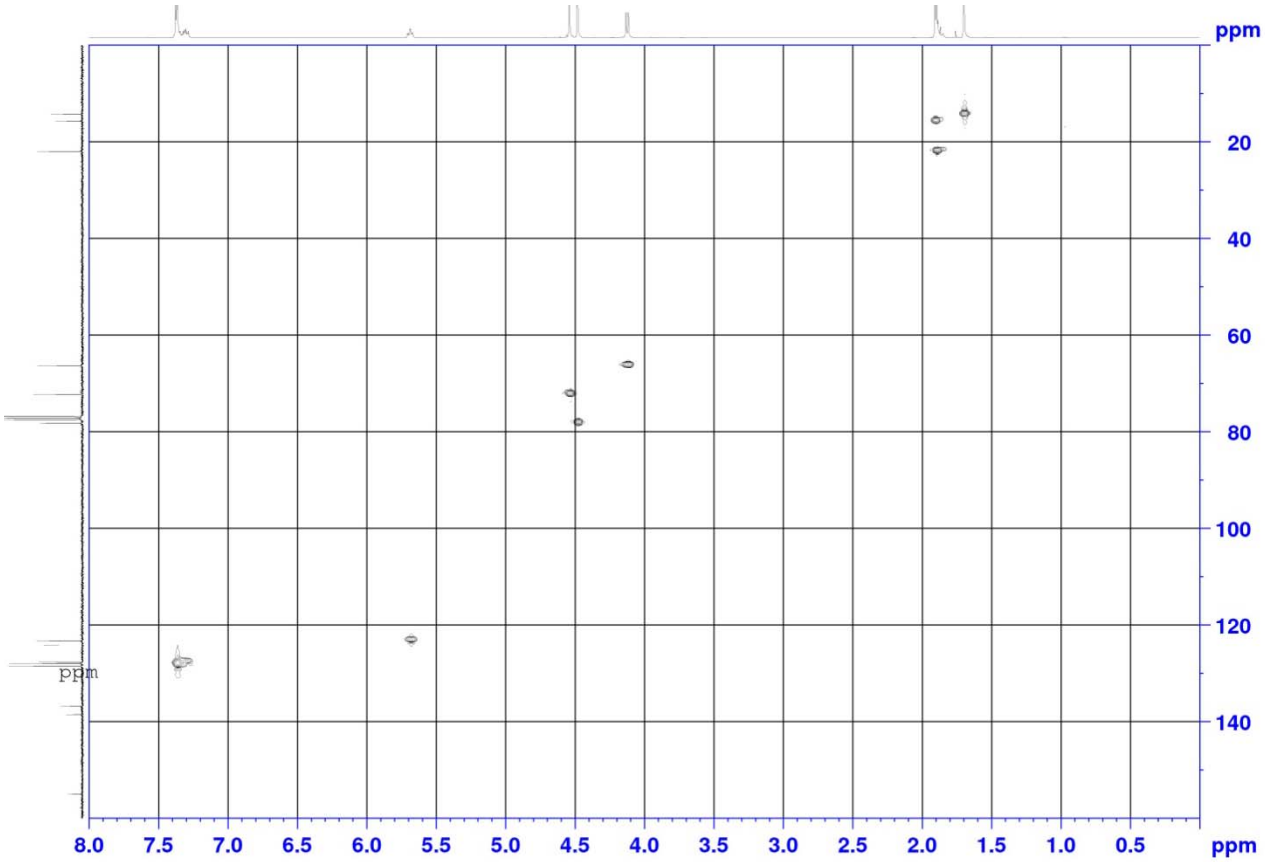

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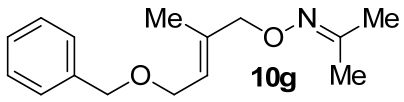
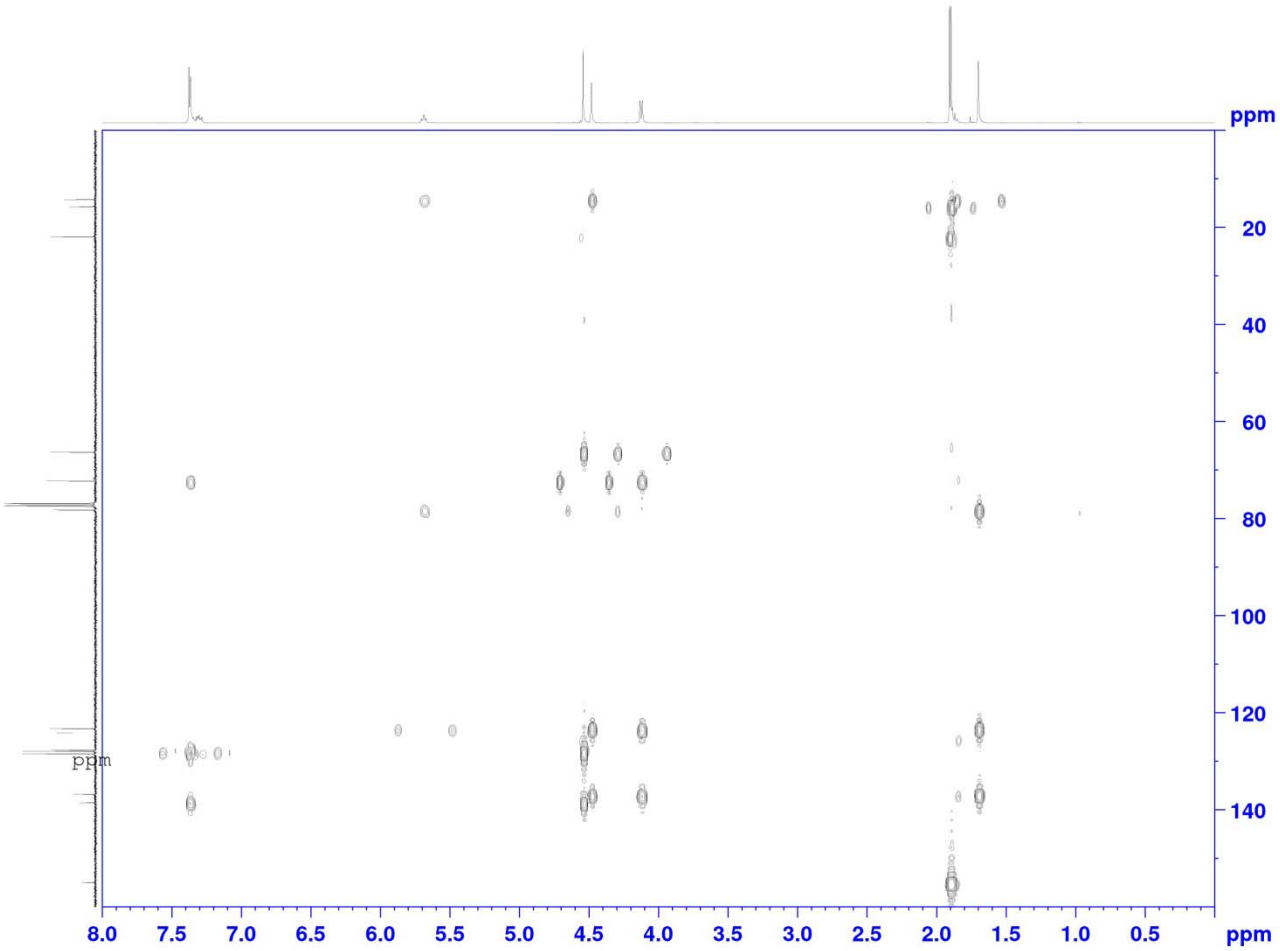
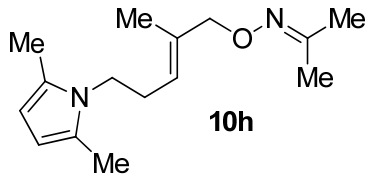


10g





10h

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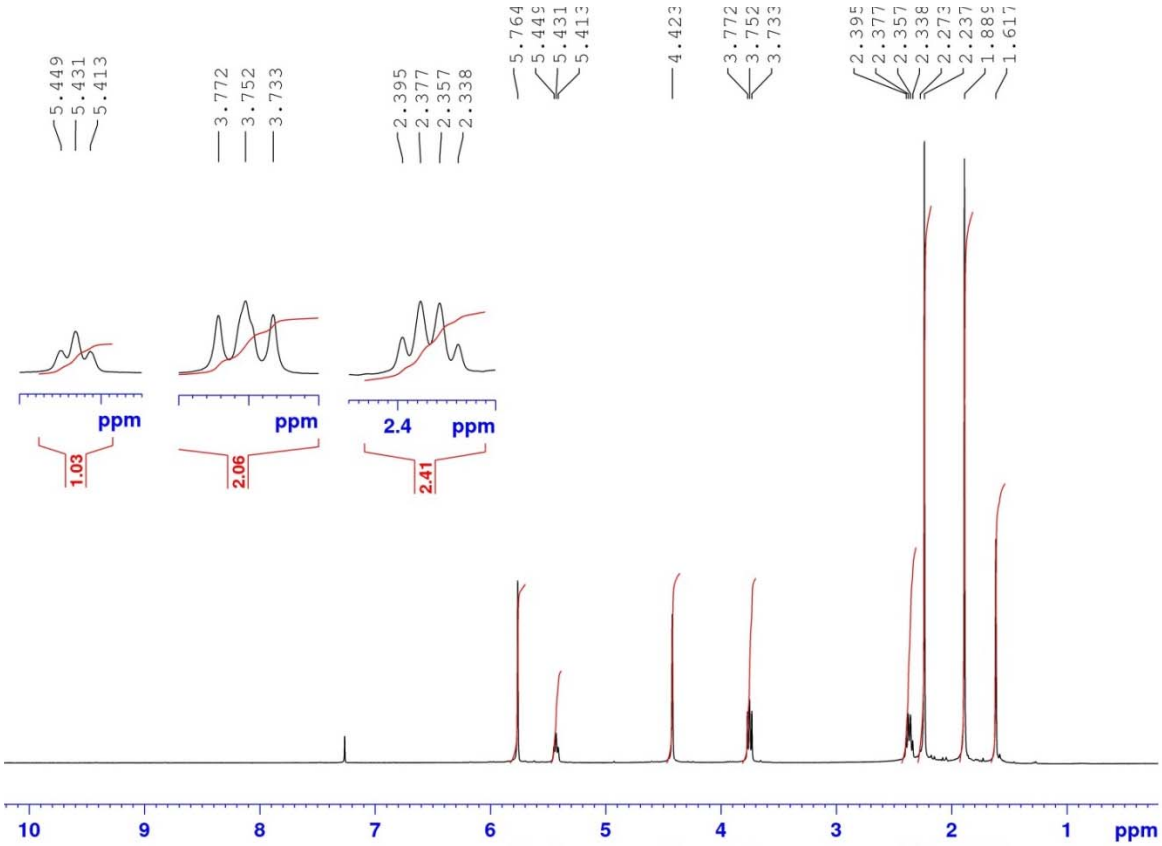
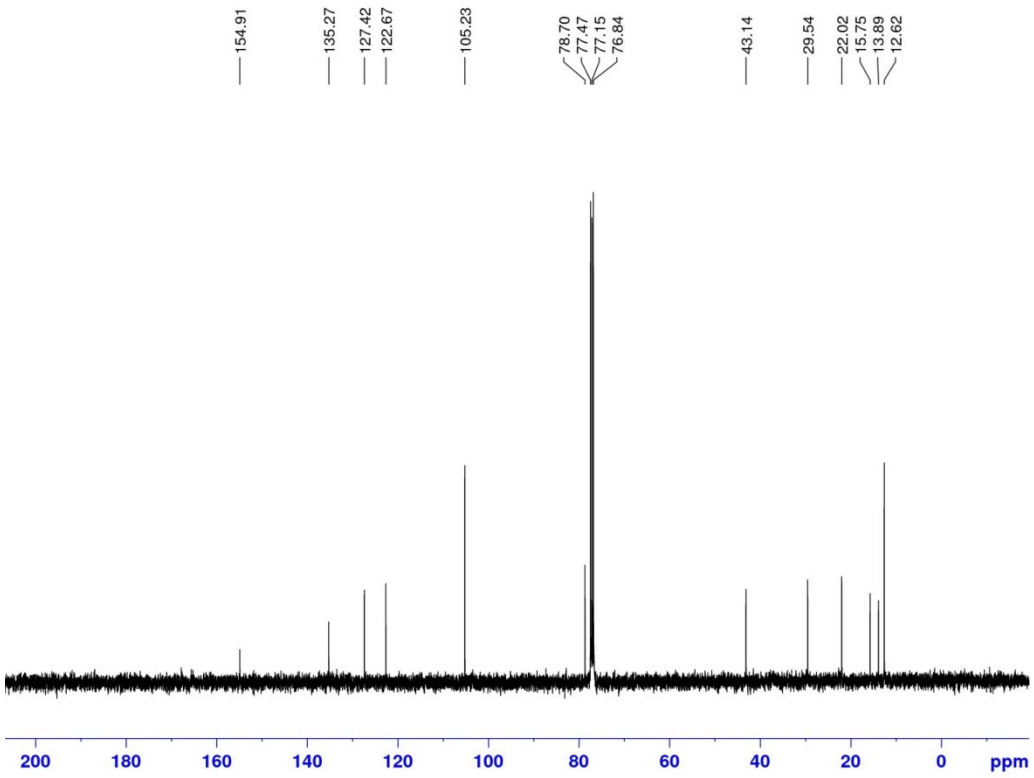
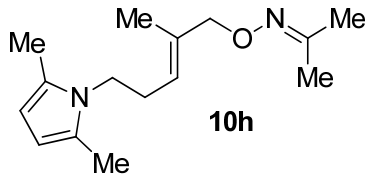


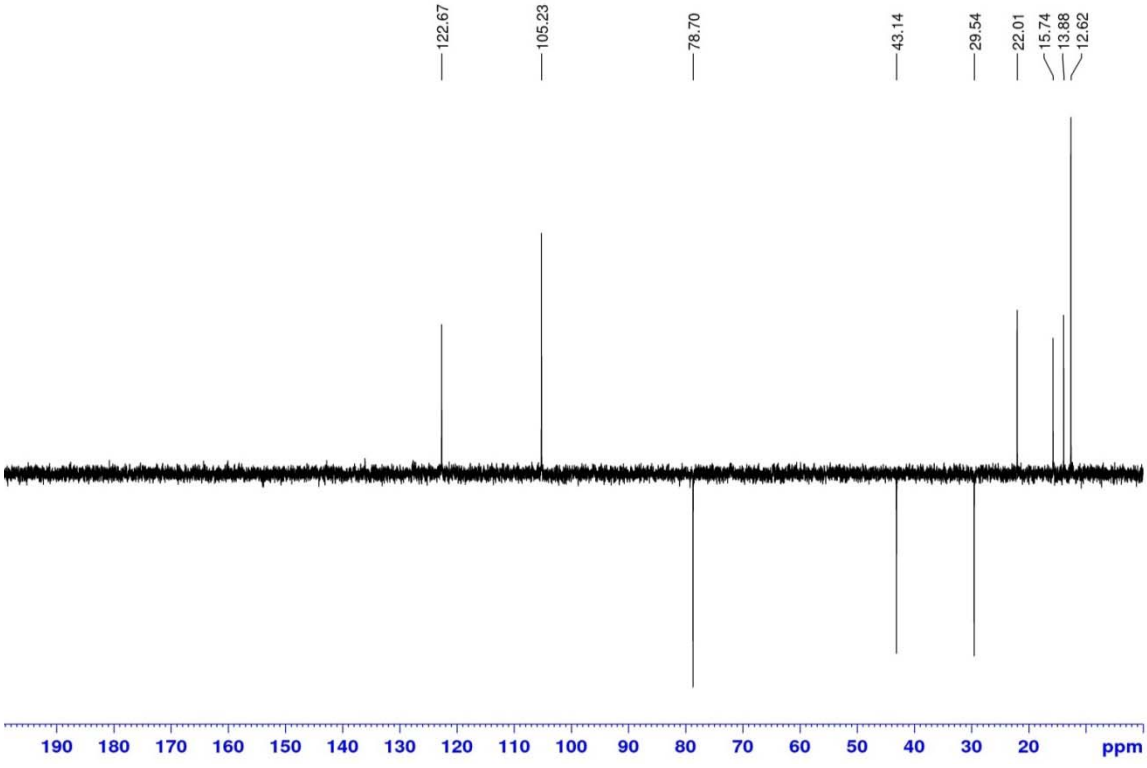
^{13}C NMR NMR



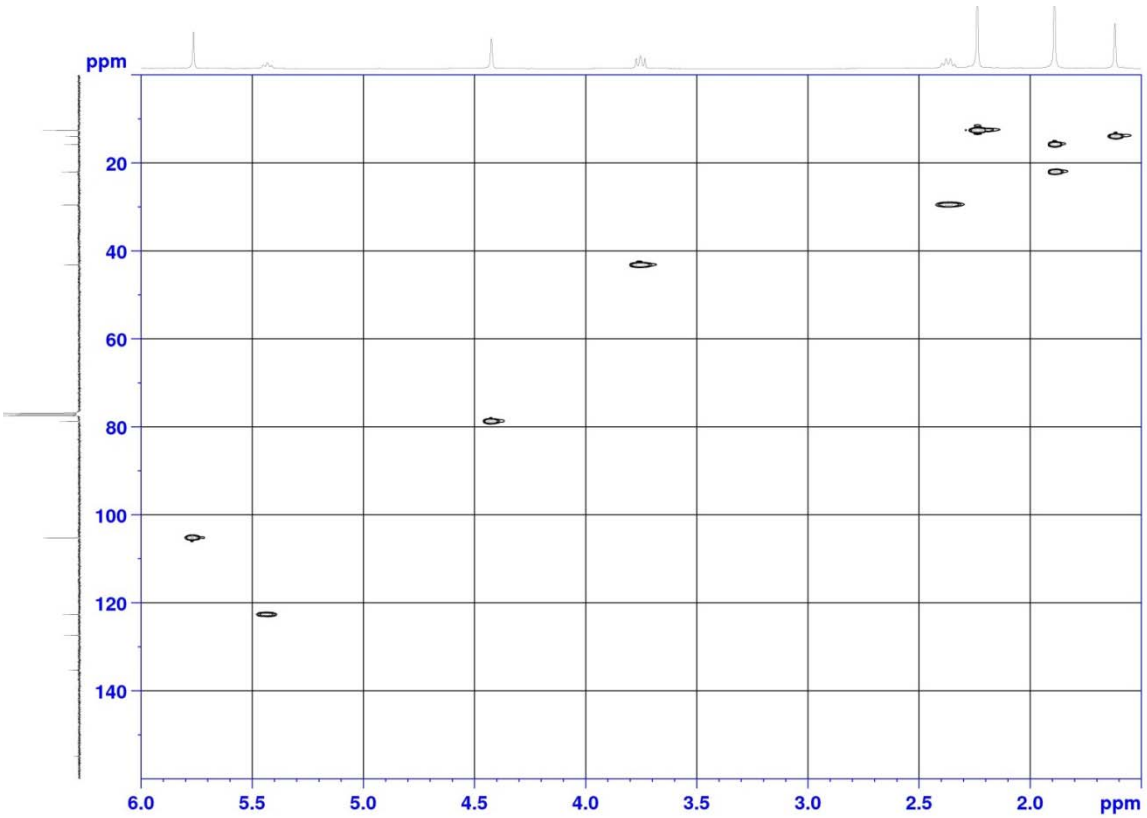


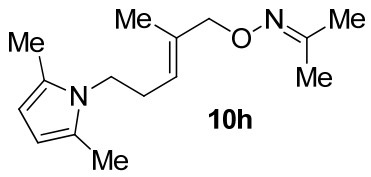
10h

^{13}C DEPT135 NMR



^{1}H-^{13}C HSQC





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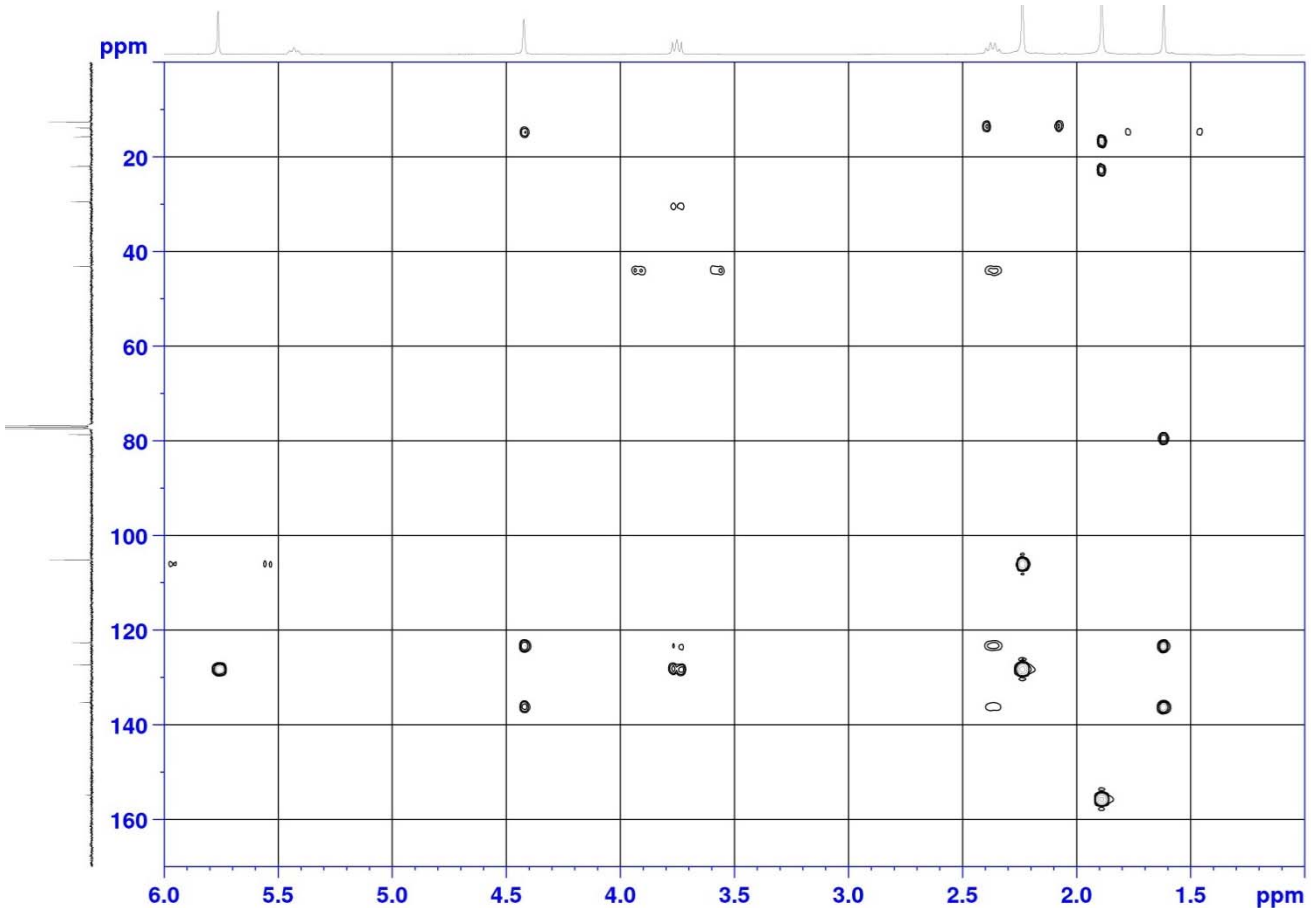

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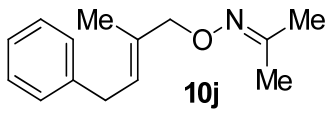

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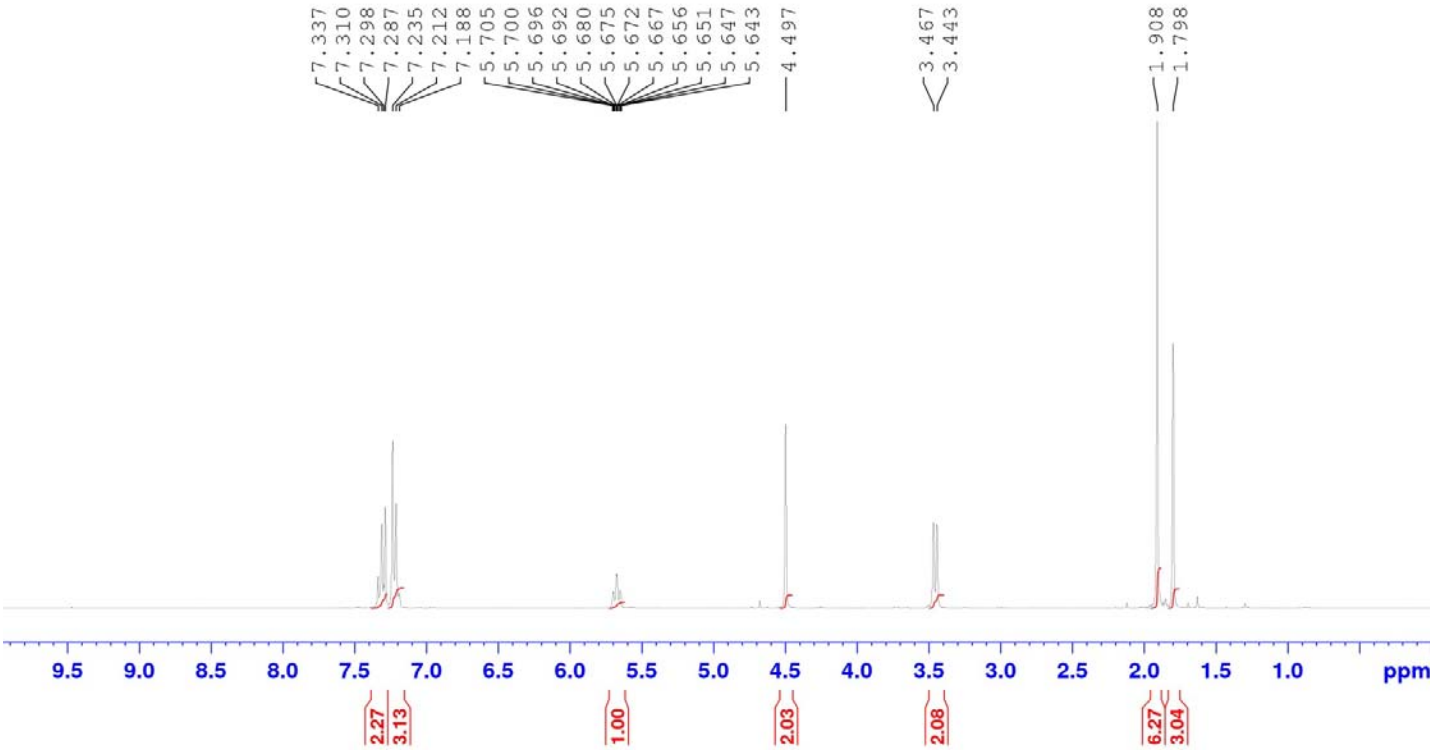
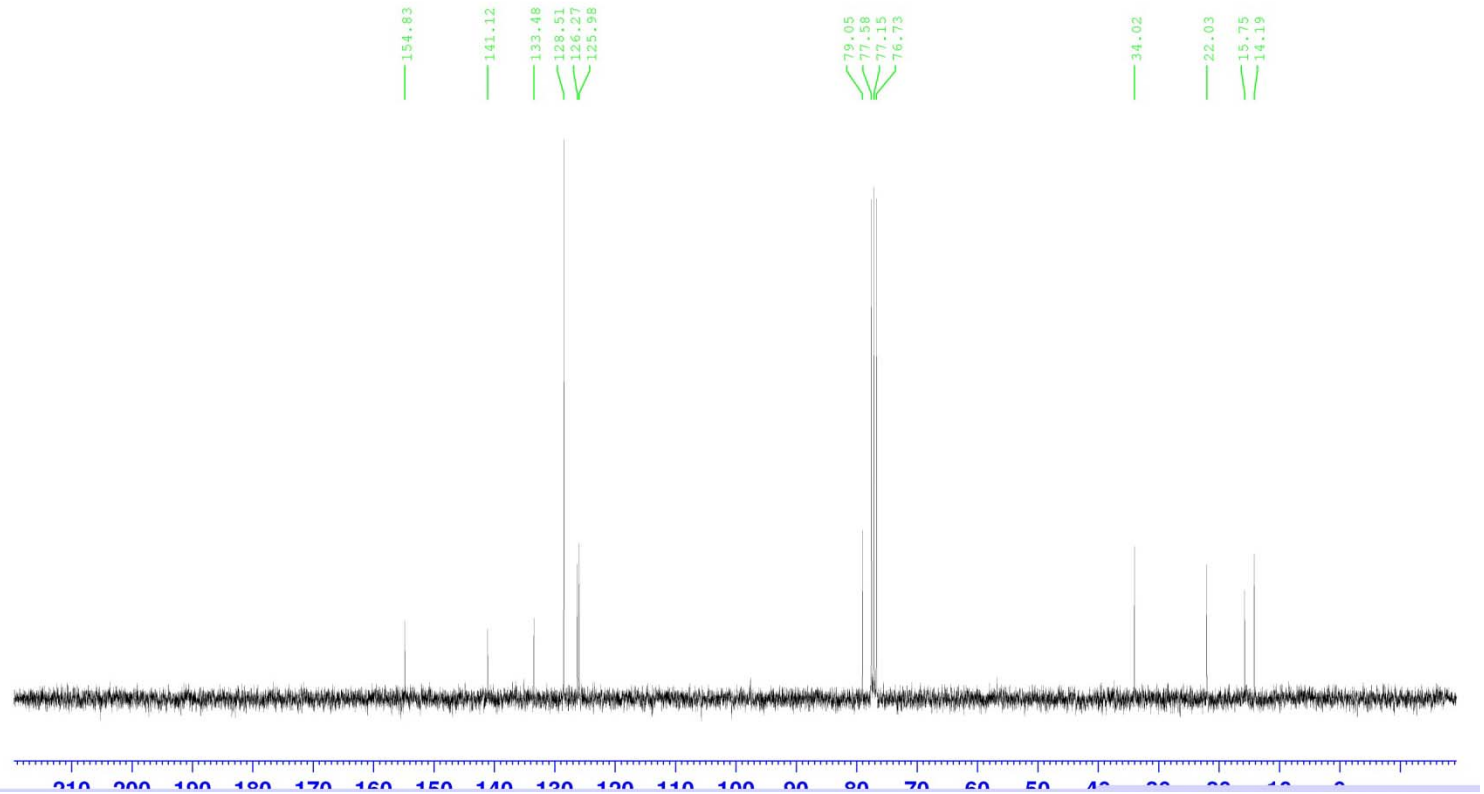
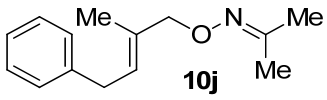


^{13}C NMR





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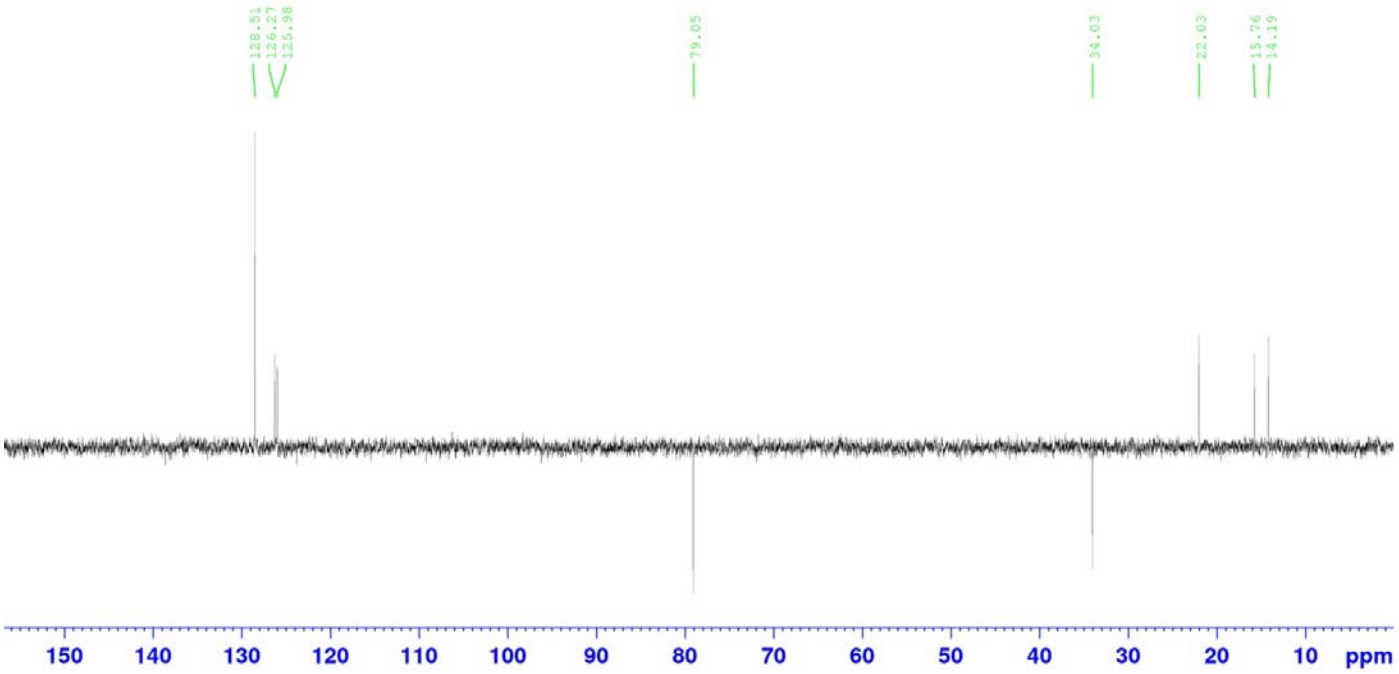
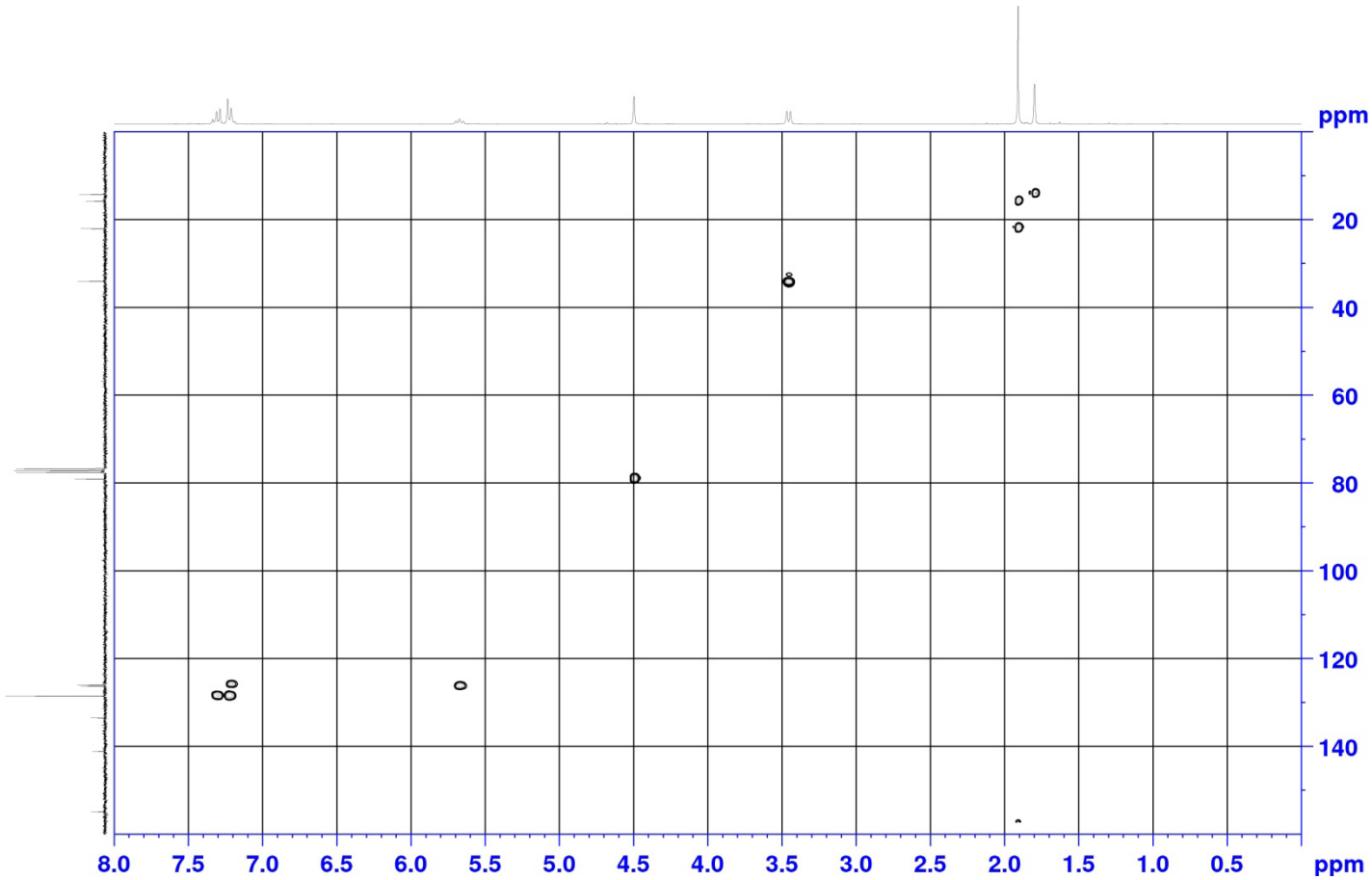
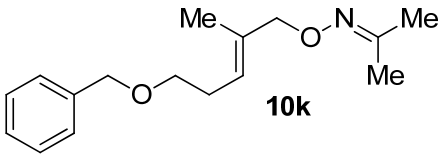
^{13}C DEPT 135 NMR



^{1}H- ^{13}C HSQC NMR





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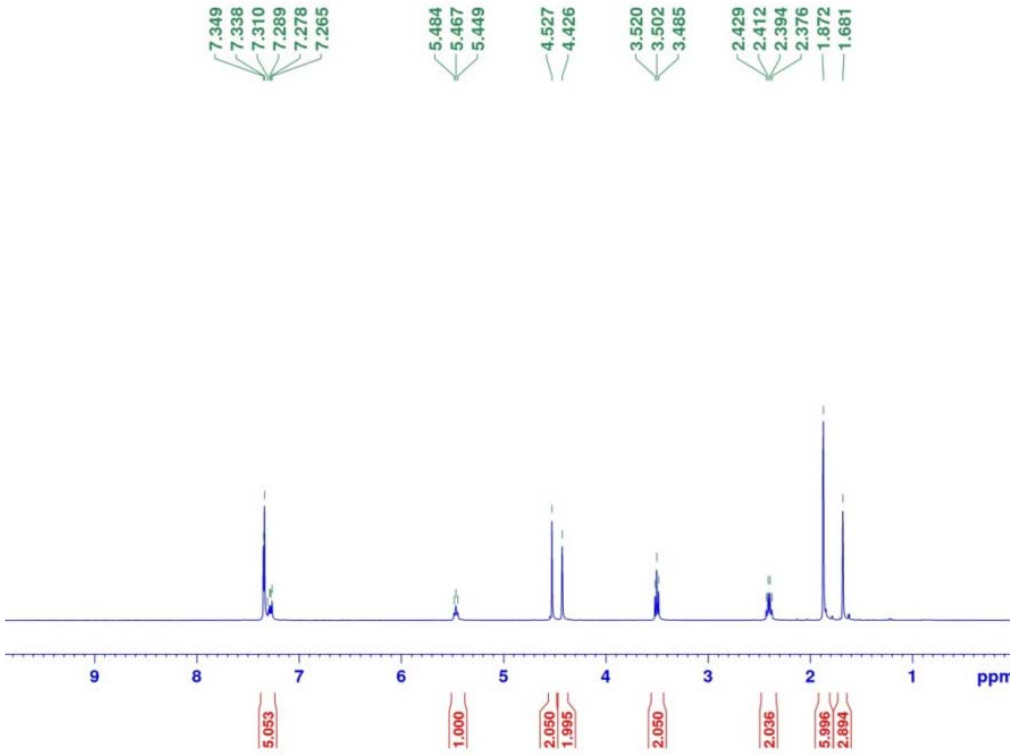

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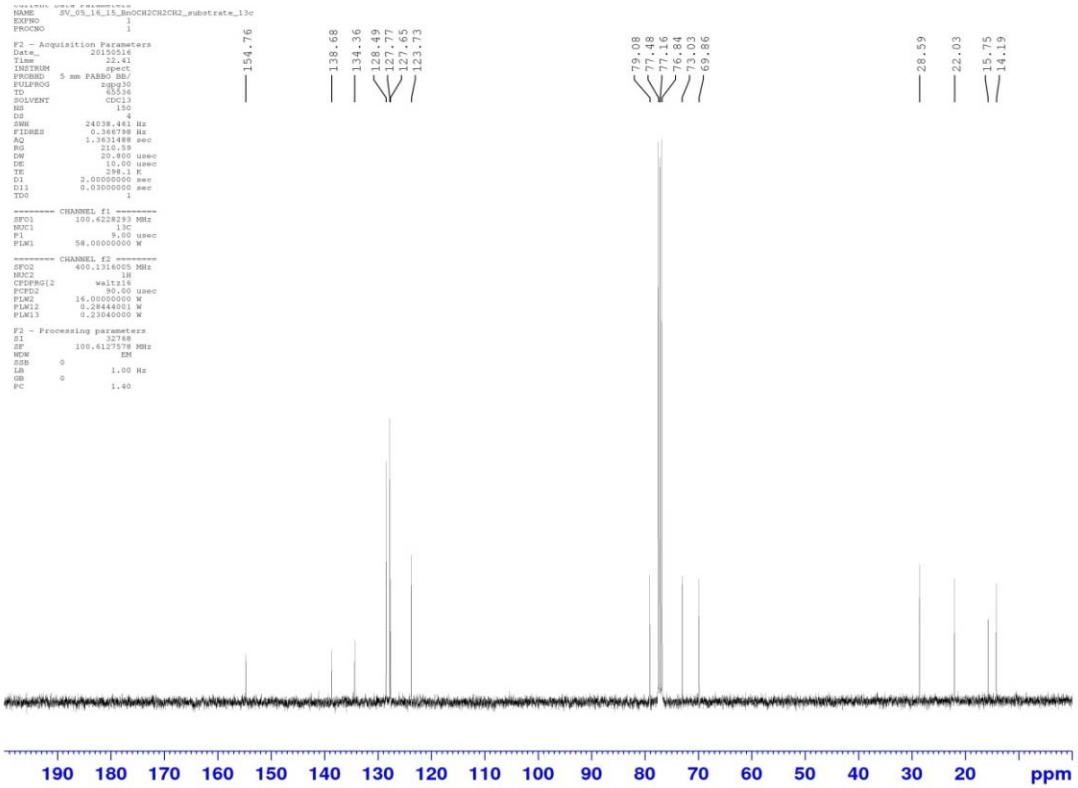

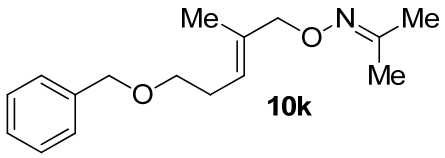

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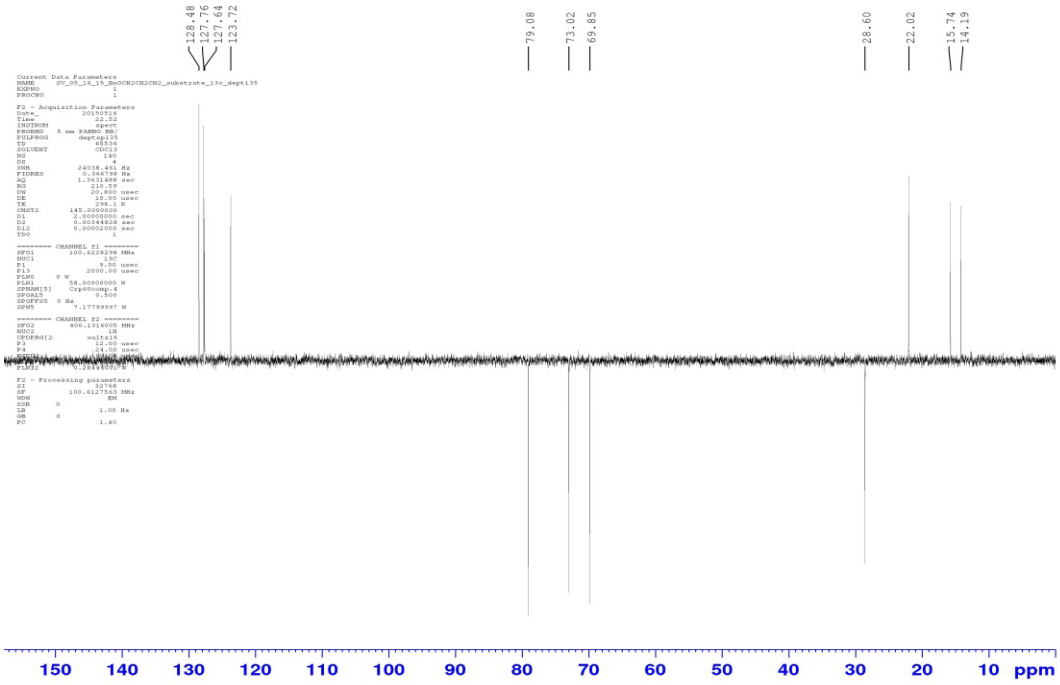
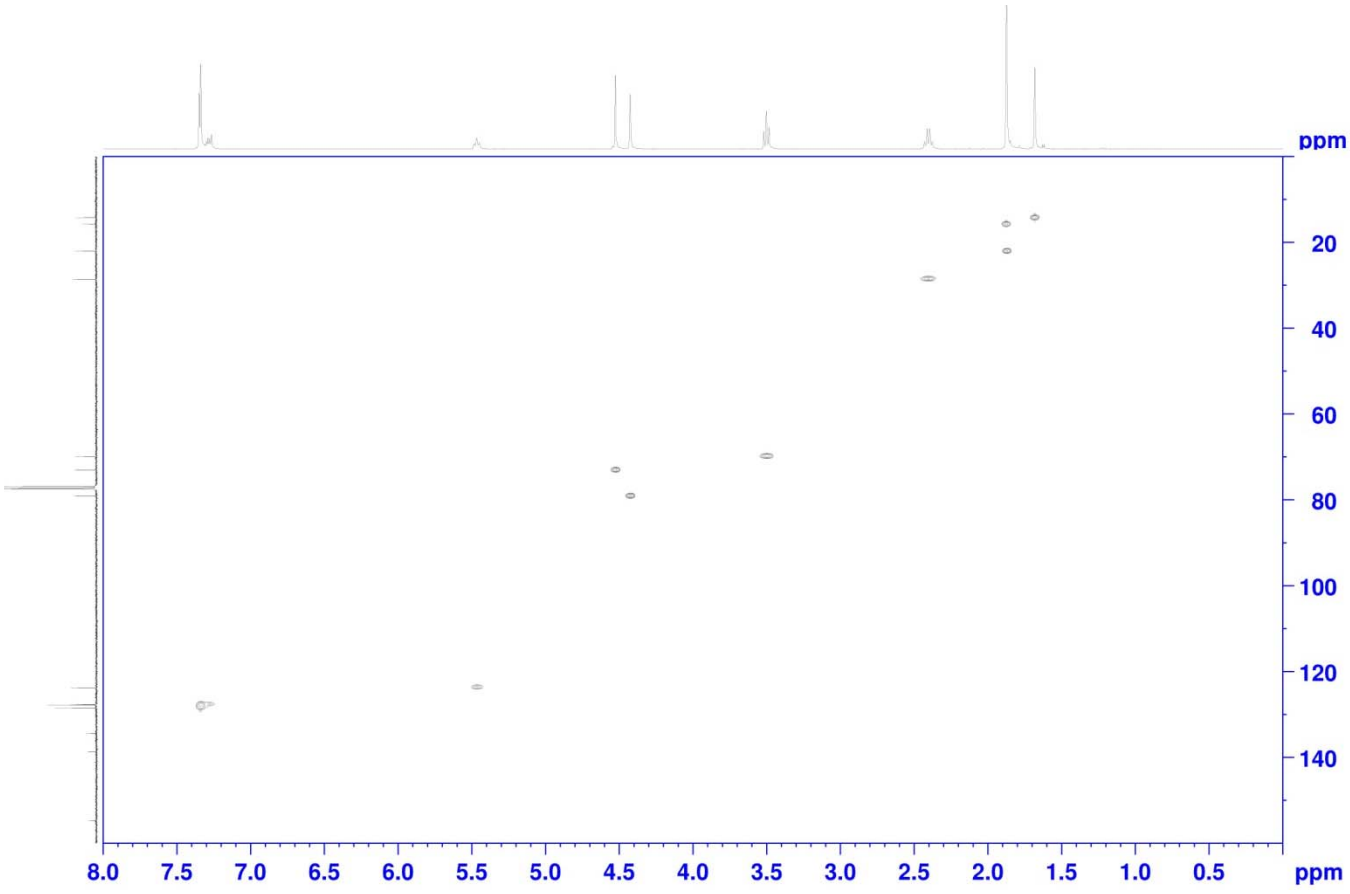
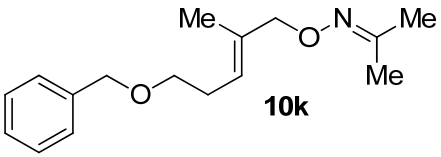


^{1}H-^{13}C HSQC





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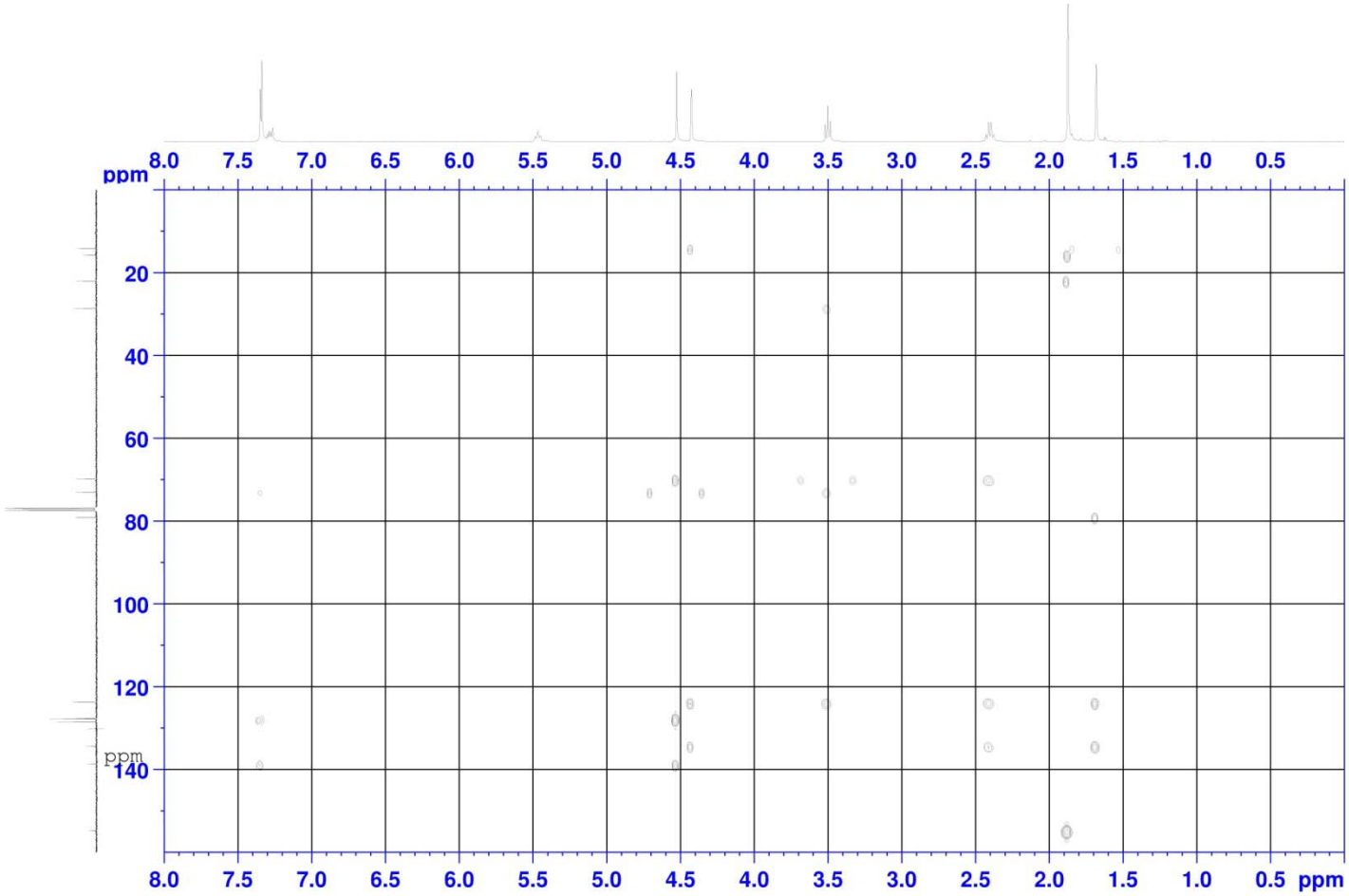

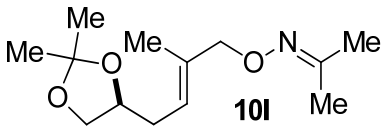

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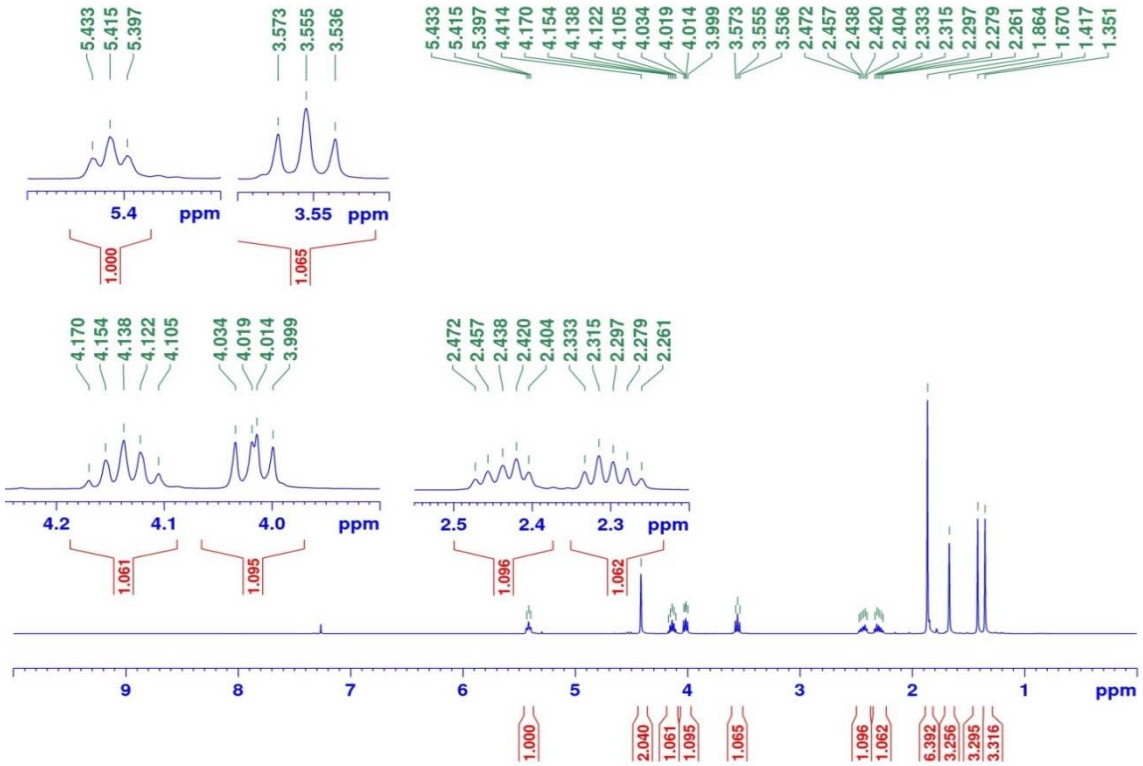

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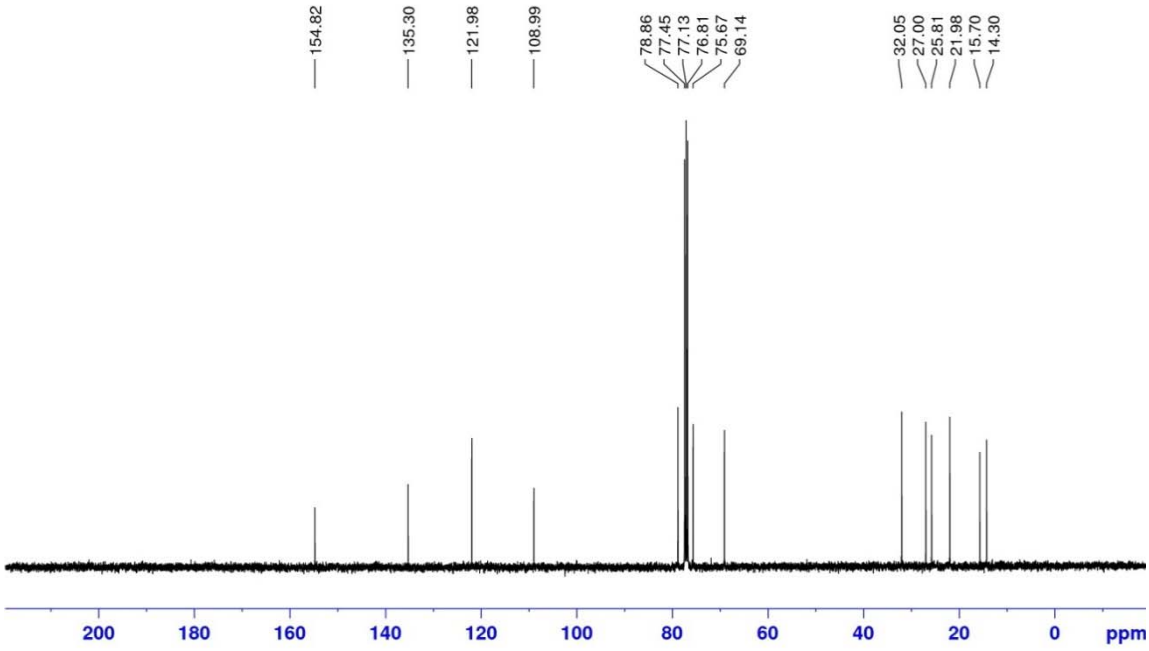
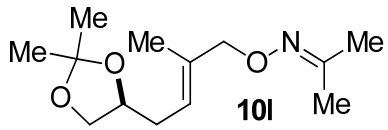
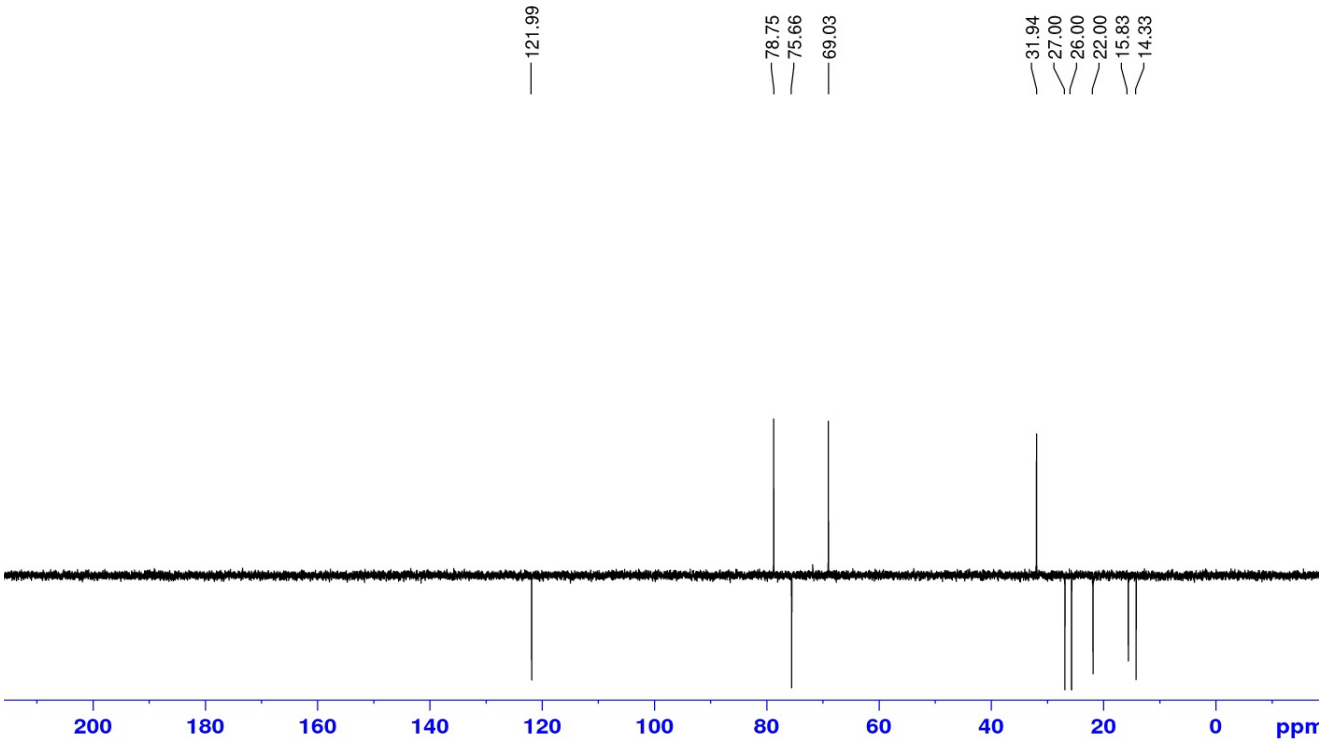


^{13}C DEPT 135 NMR





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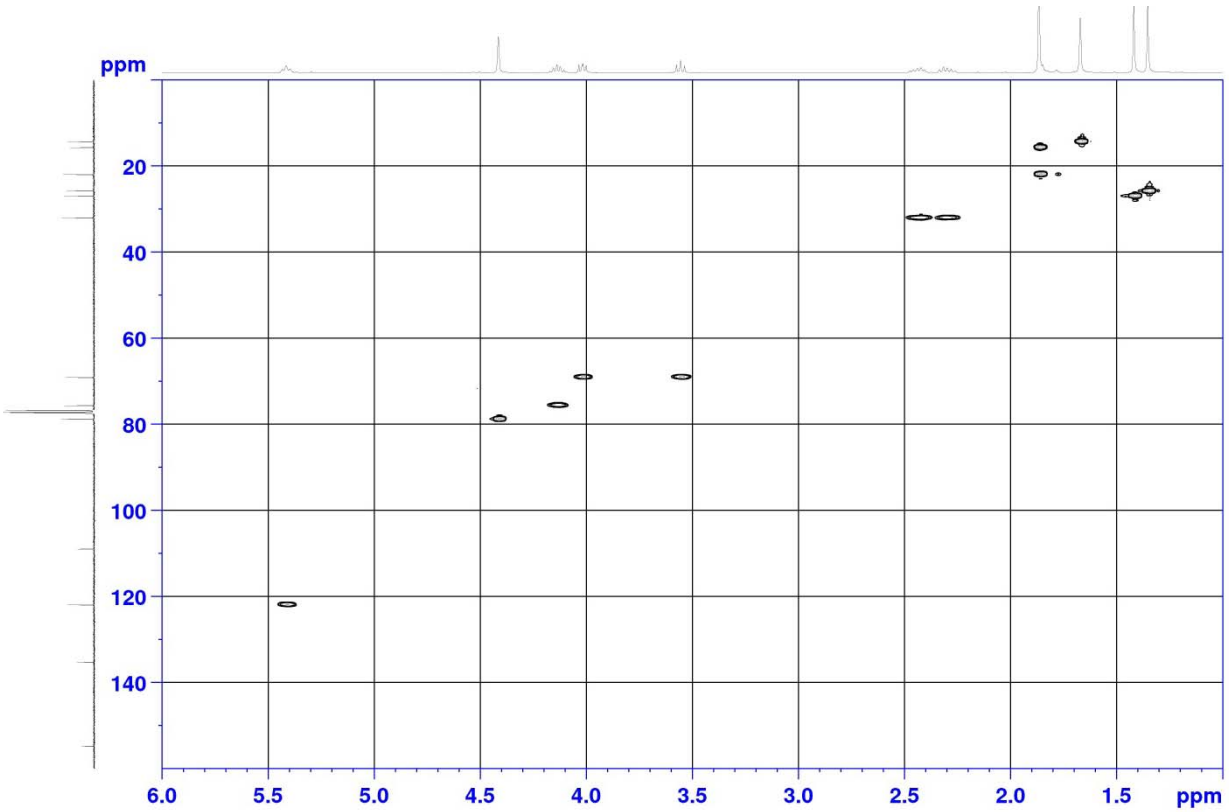
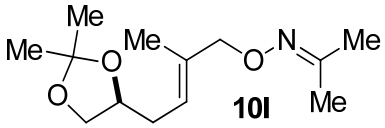


^{1}H-^{13}C HMBC NMR



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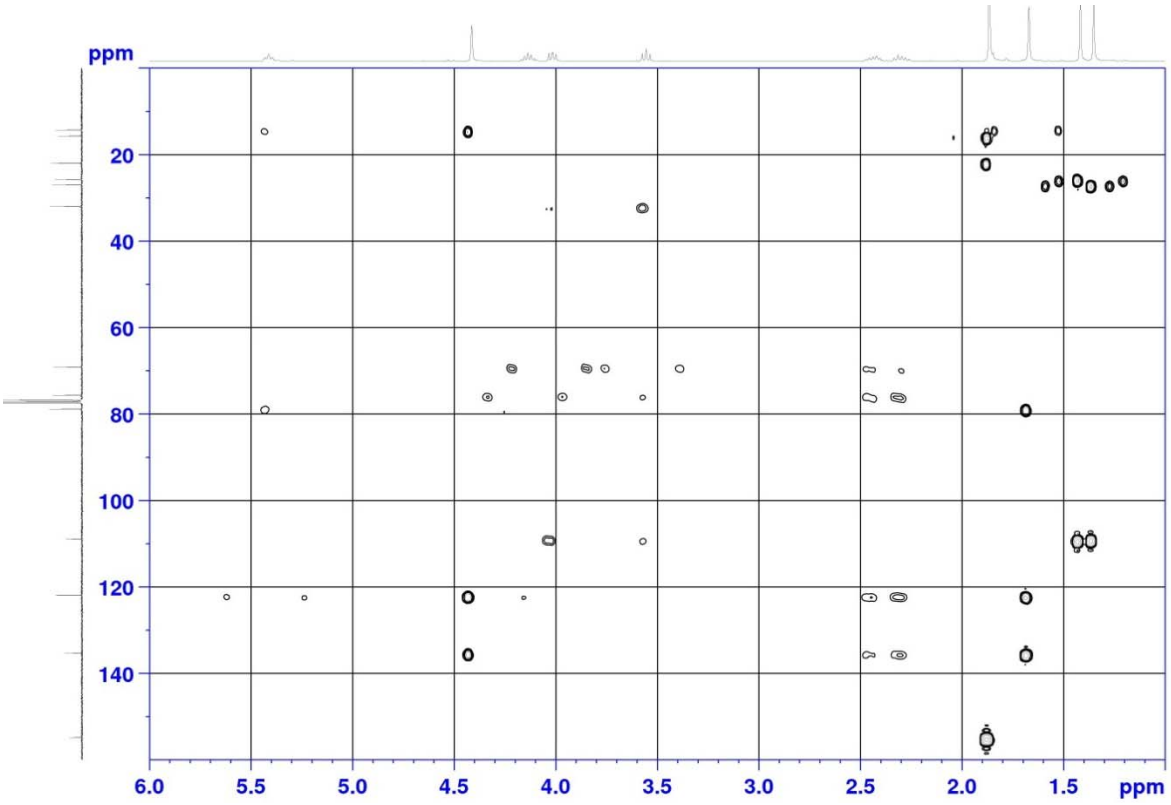

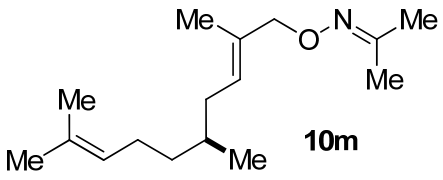

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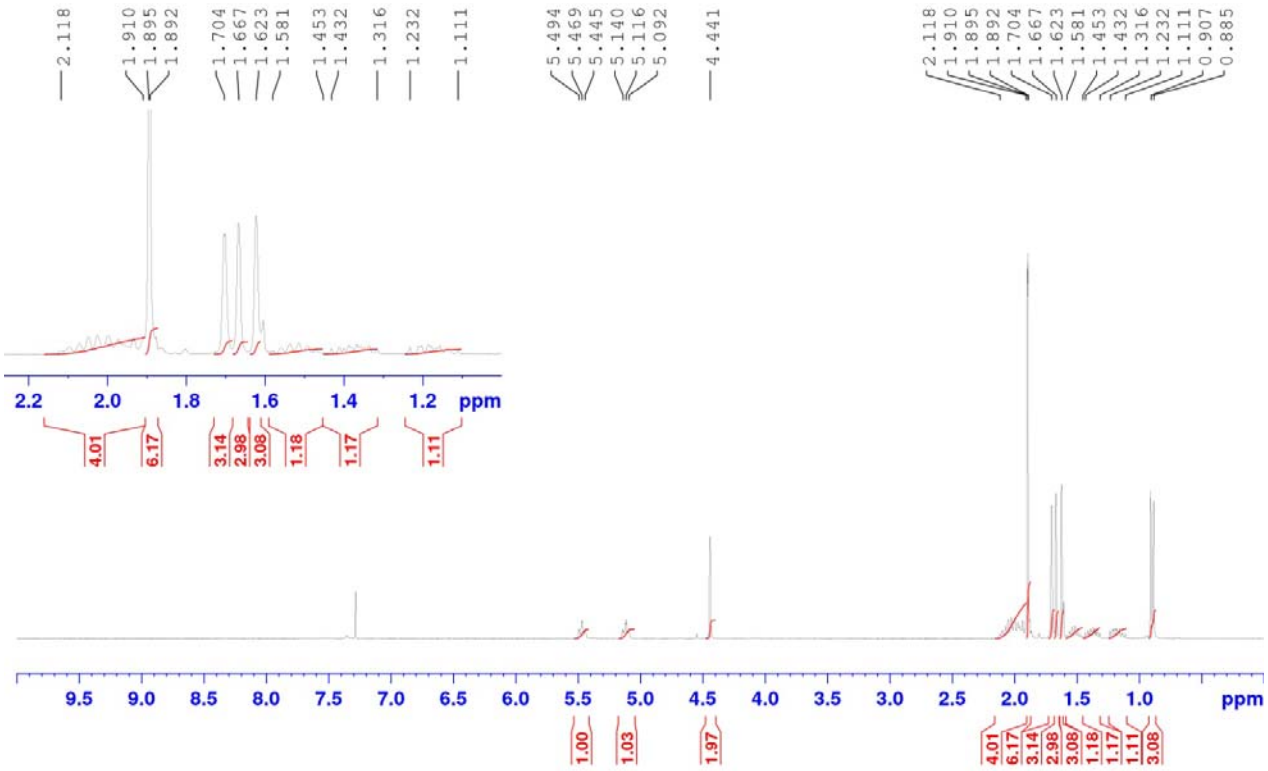
^{1}H NMR



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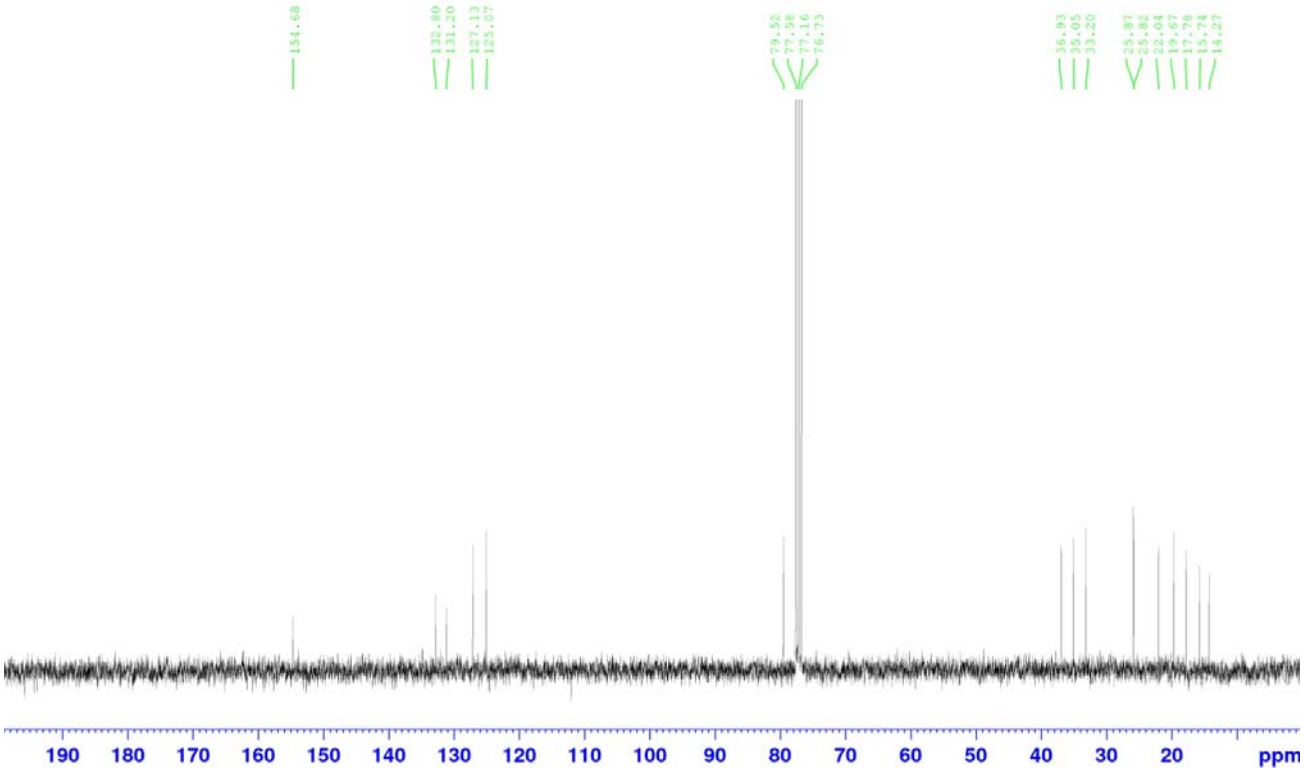

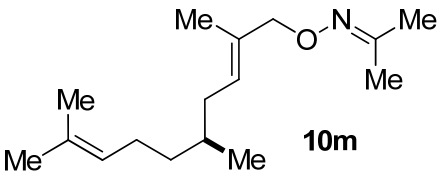

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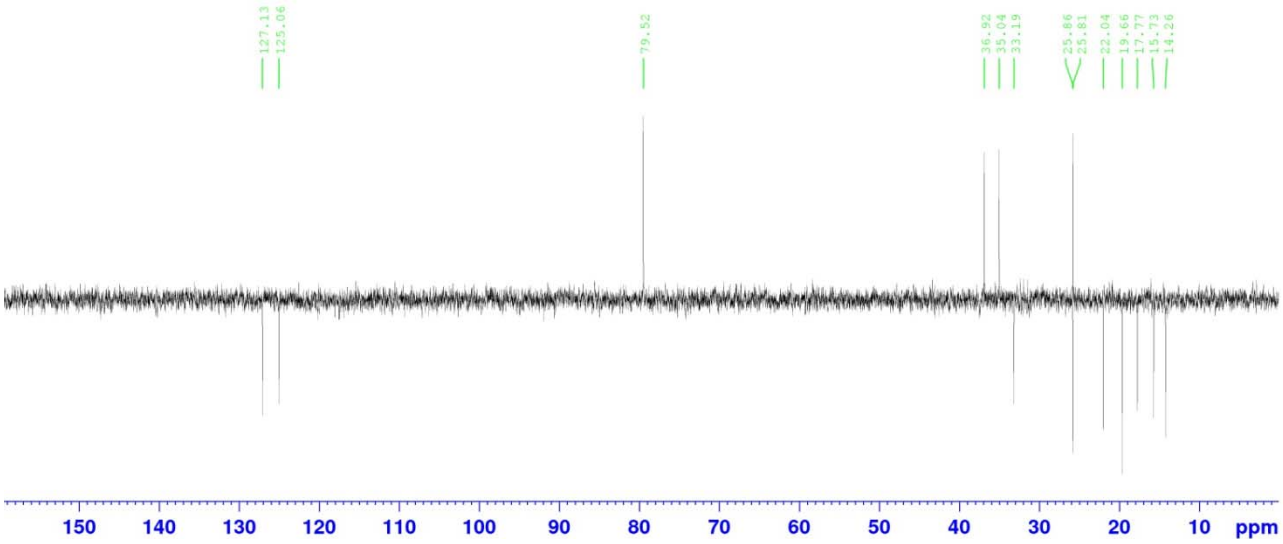
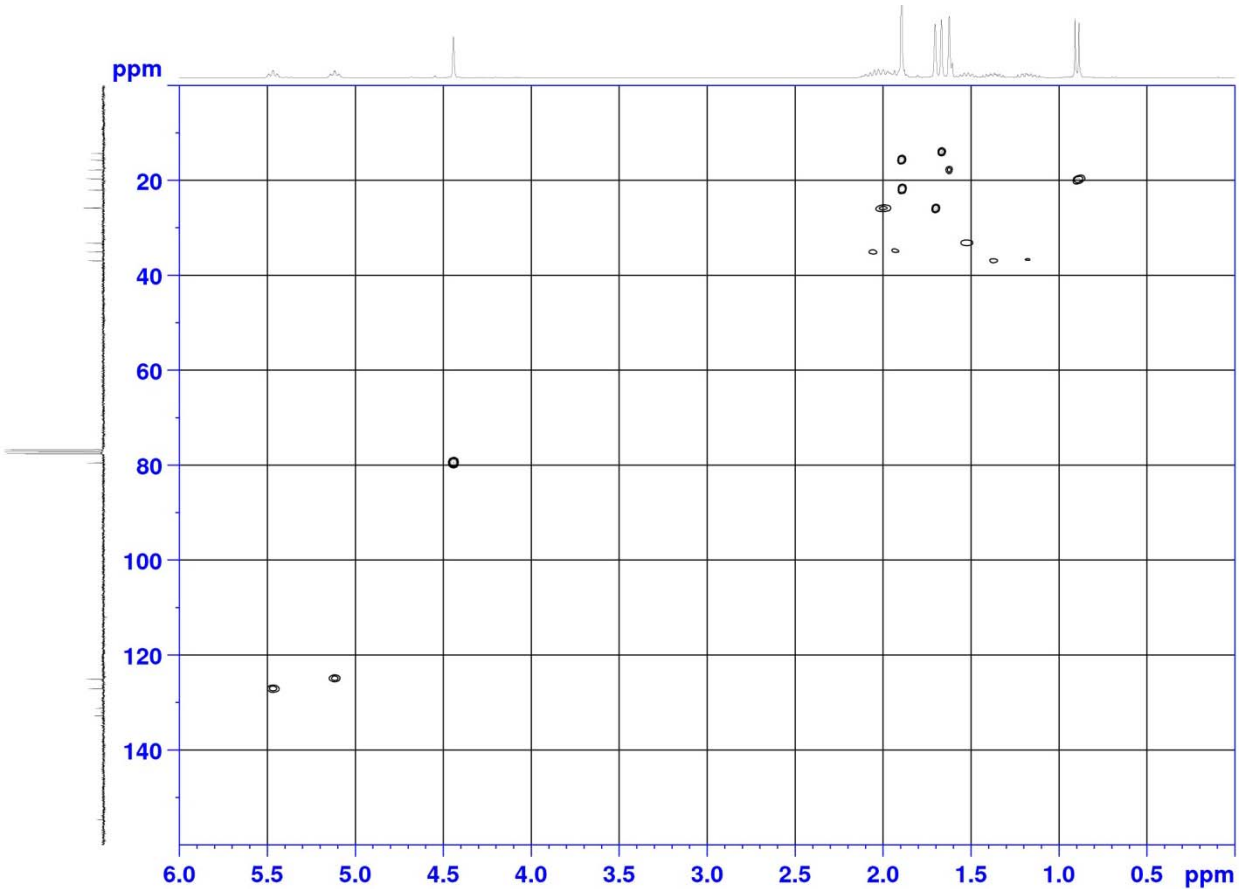
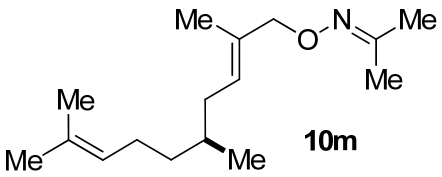
^{13}C DEPT 135 NMR



^{1}H - ^{13}C HSQC NMR



^{1}H - ^{13}C HMBC 135 NMR



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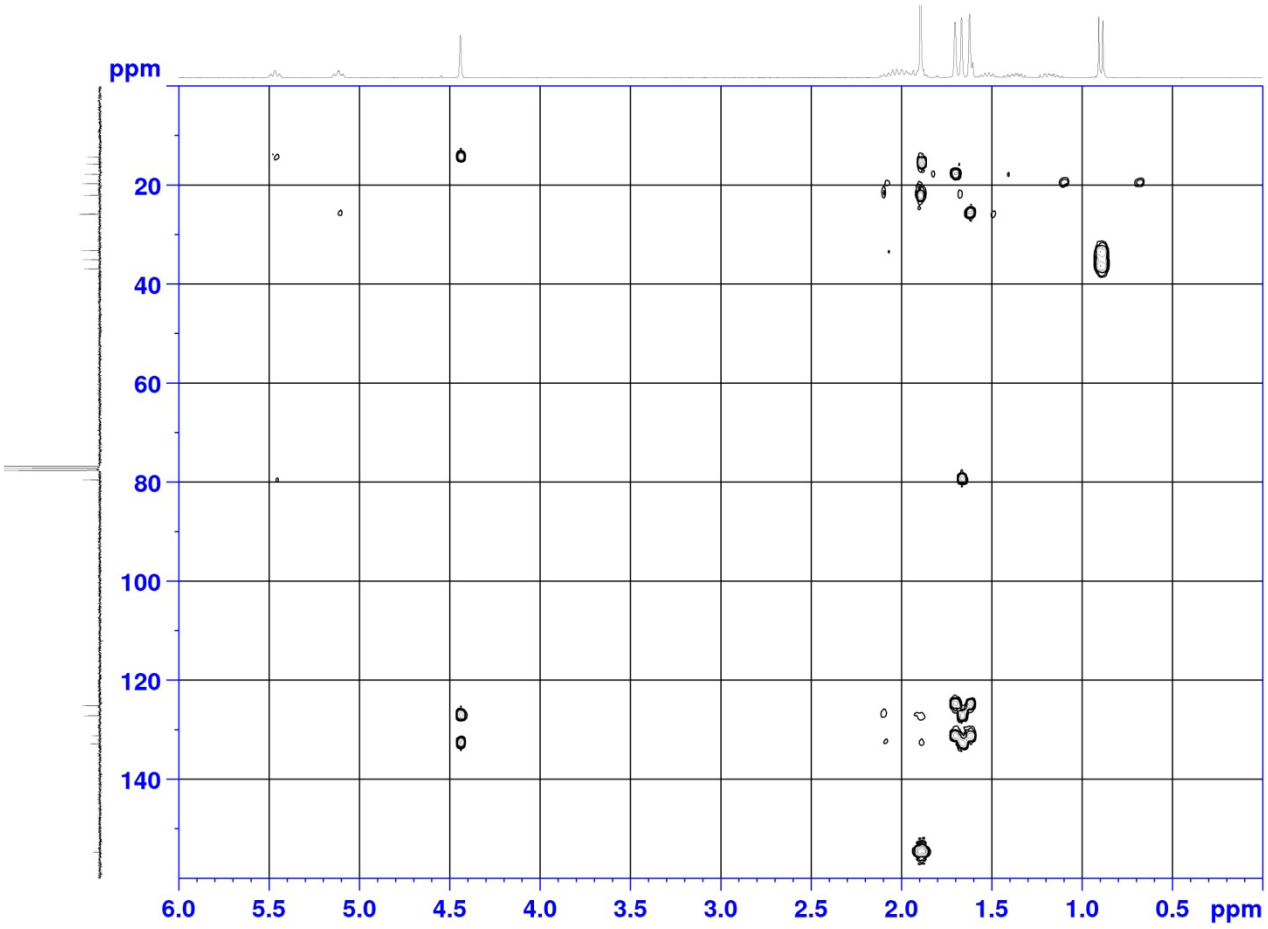

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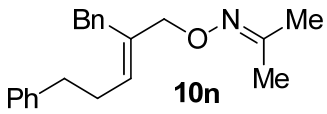

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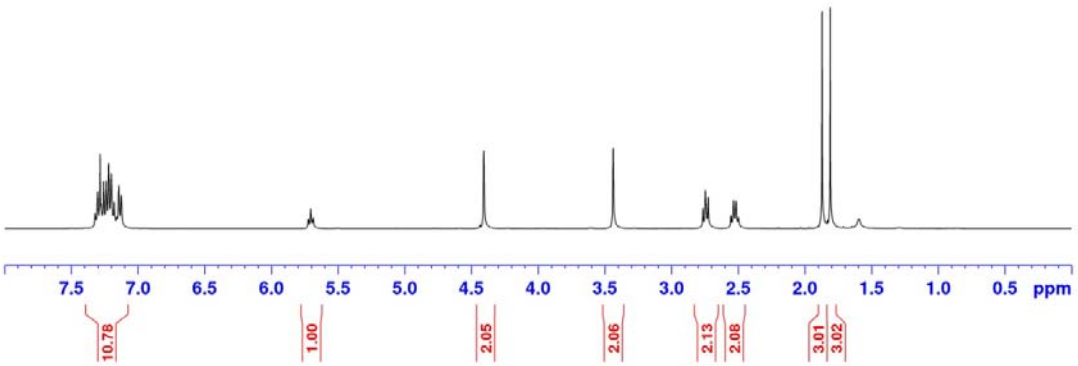

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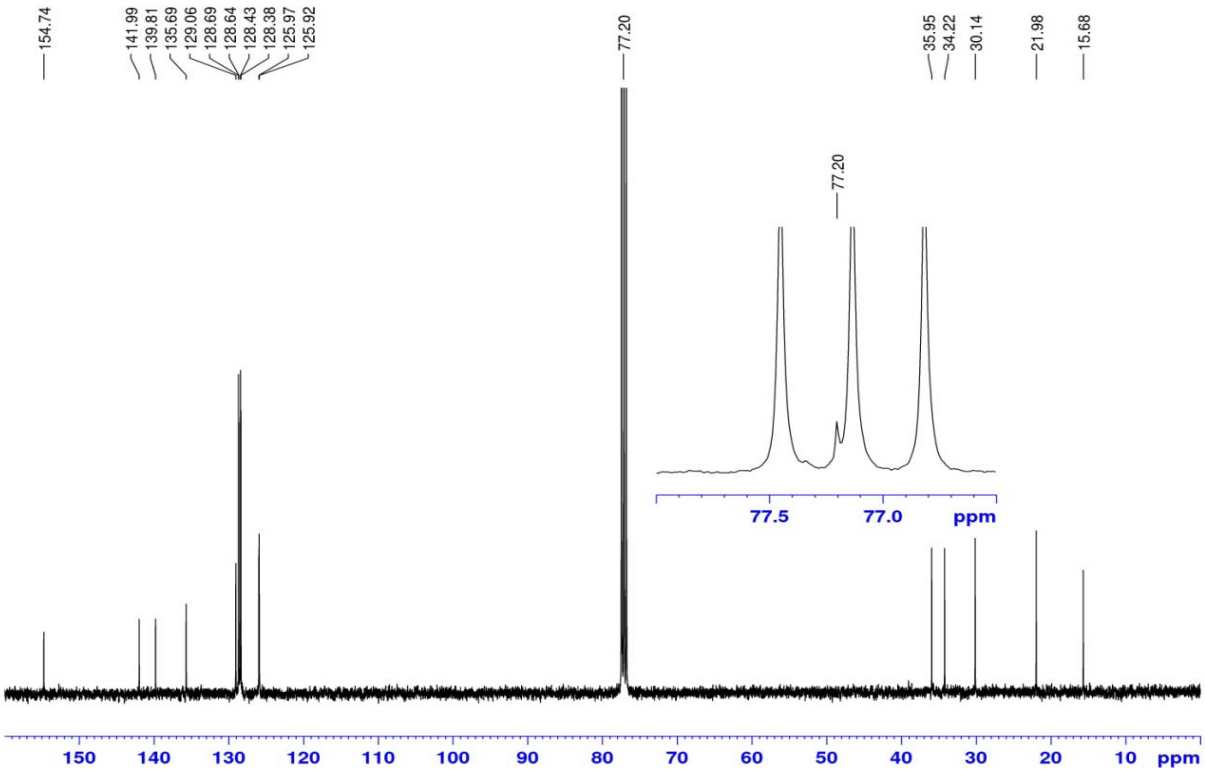
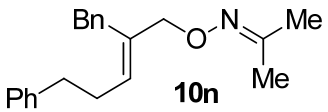


^{13}C DEPT 135 NMR



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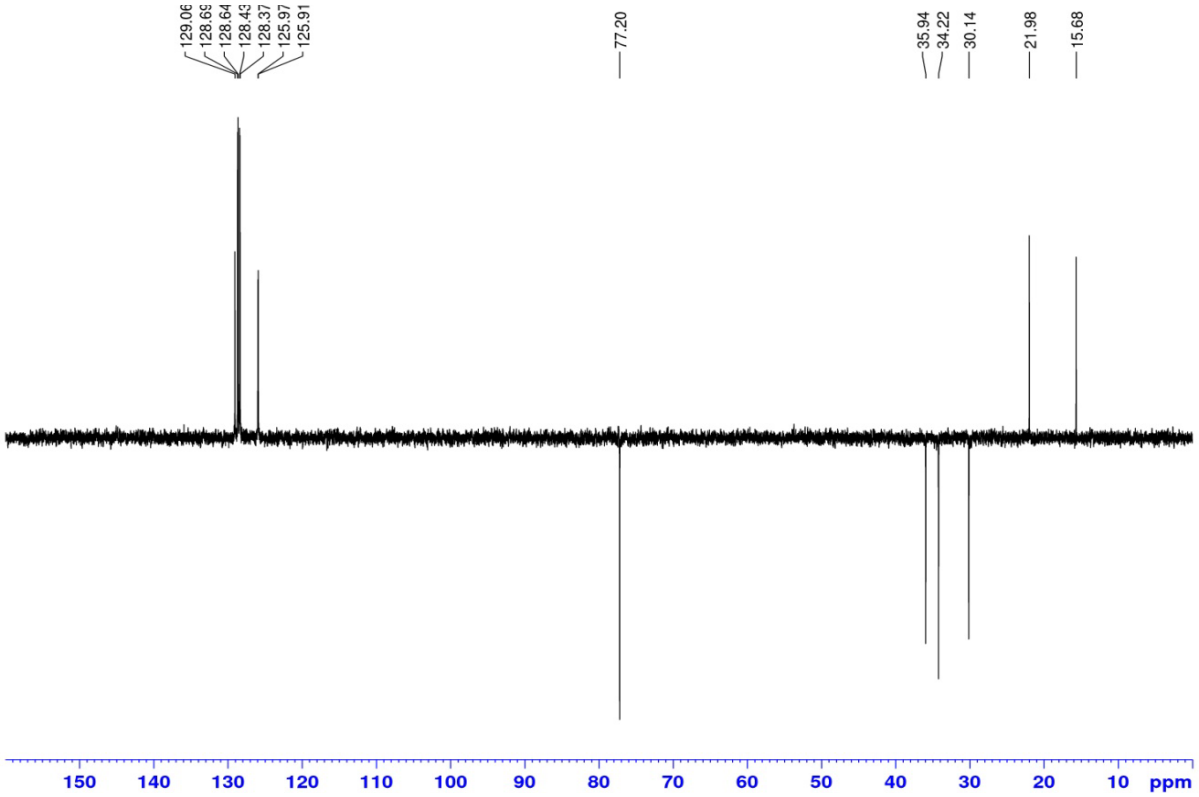
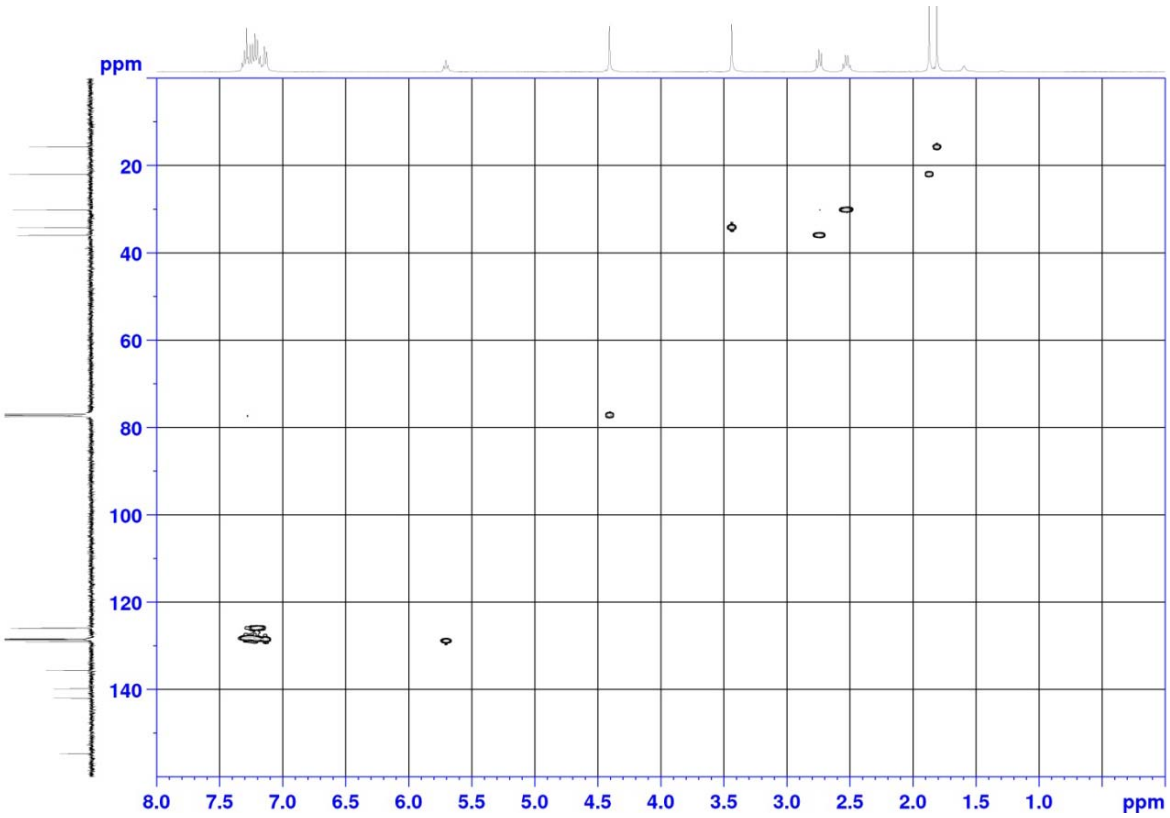
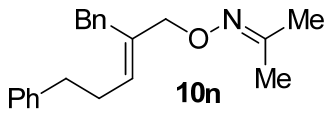


^{1}H-^{13}C HSQC NMR



^{1}H-^{13}C HMBC NMR



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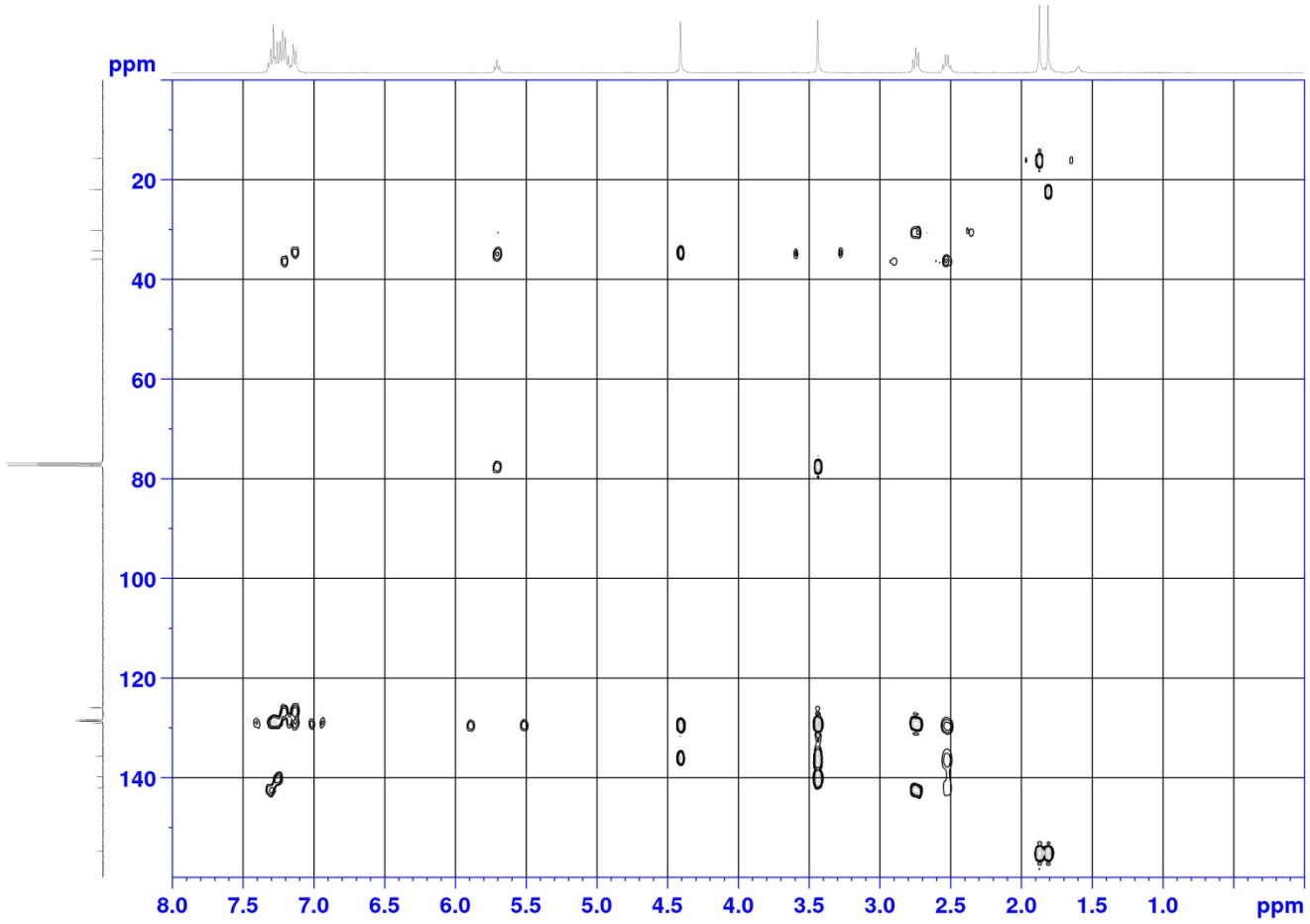

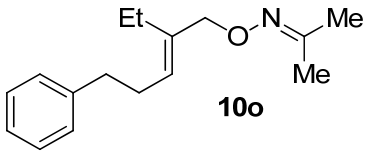

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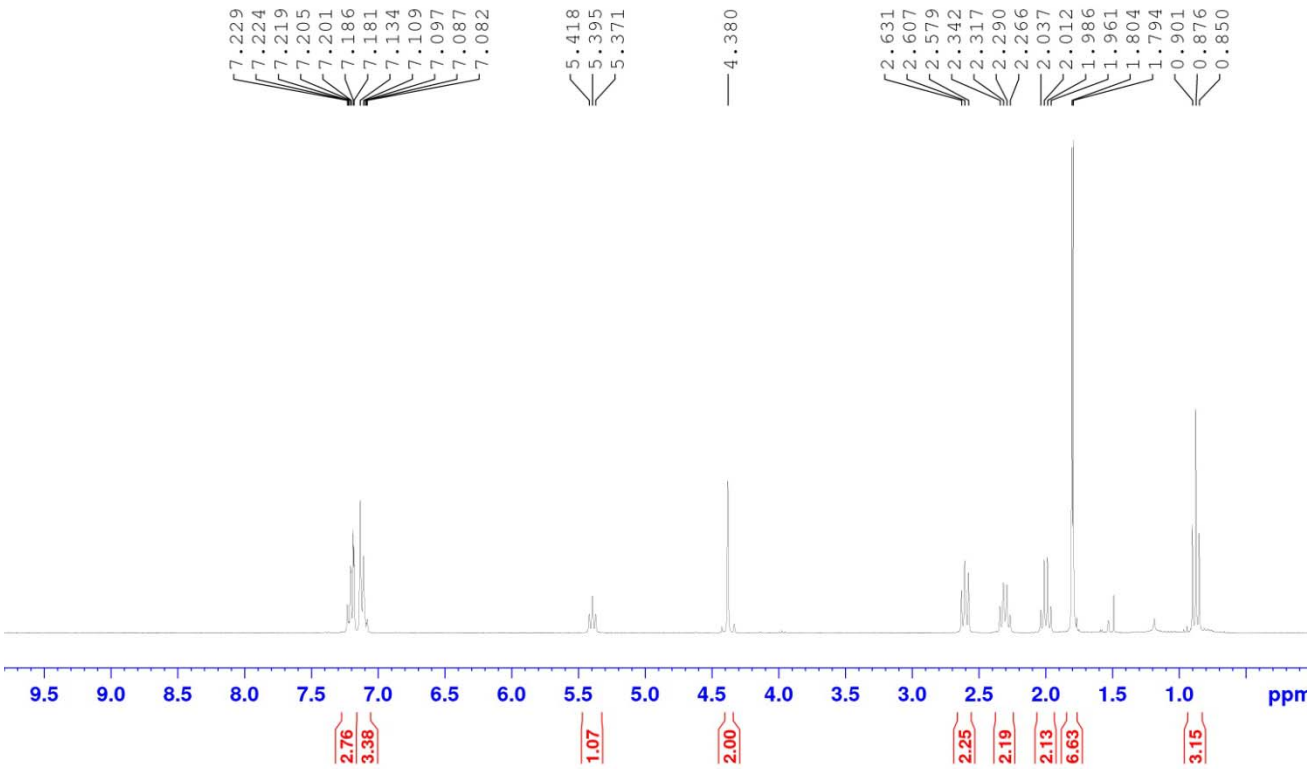
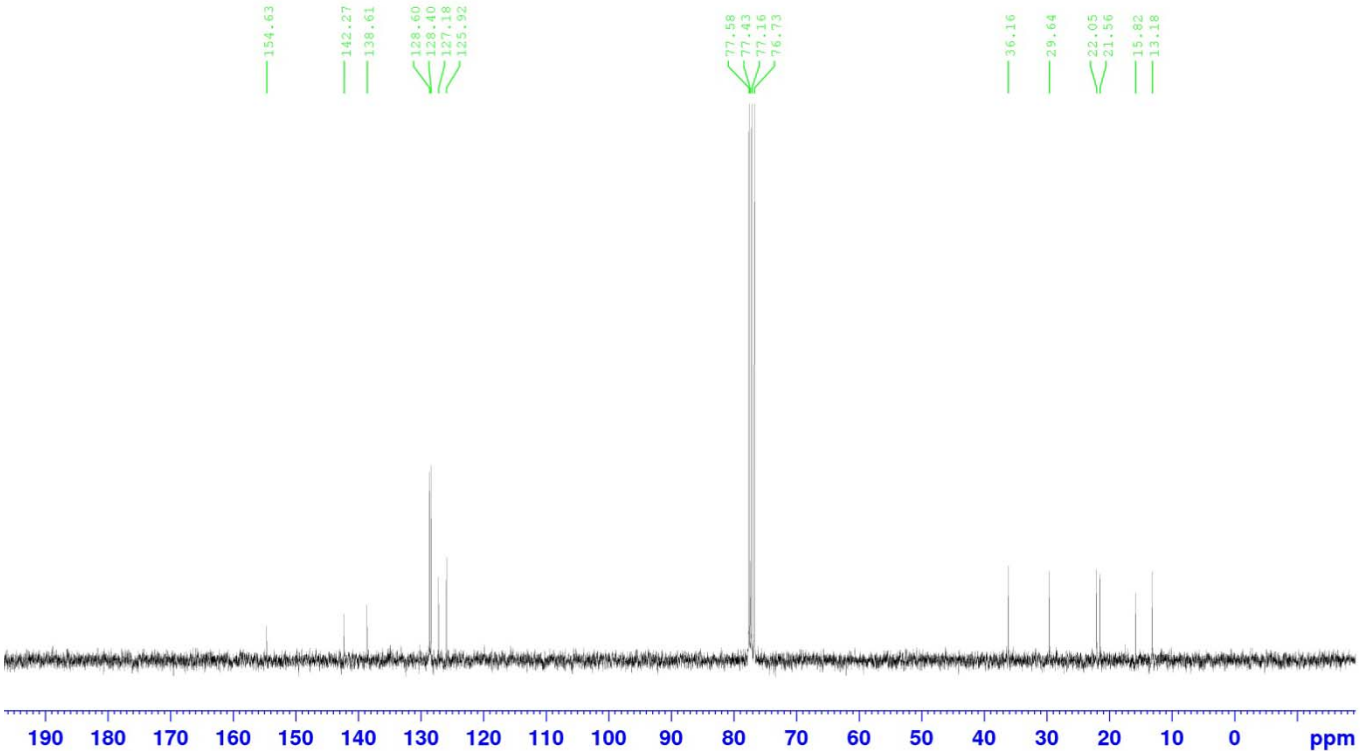
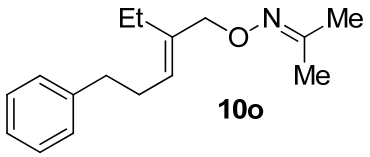
^{1}H NMR



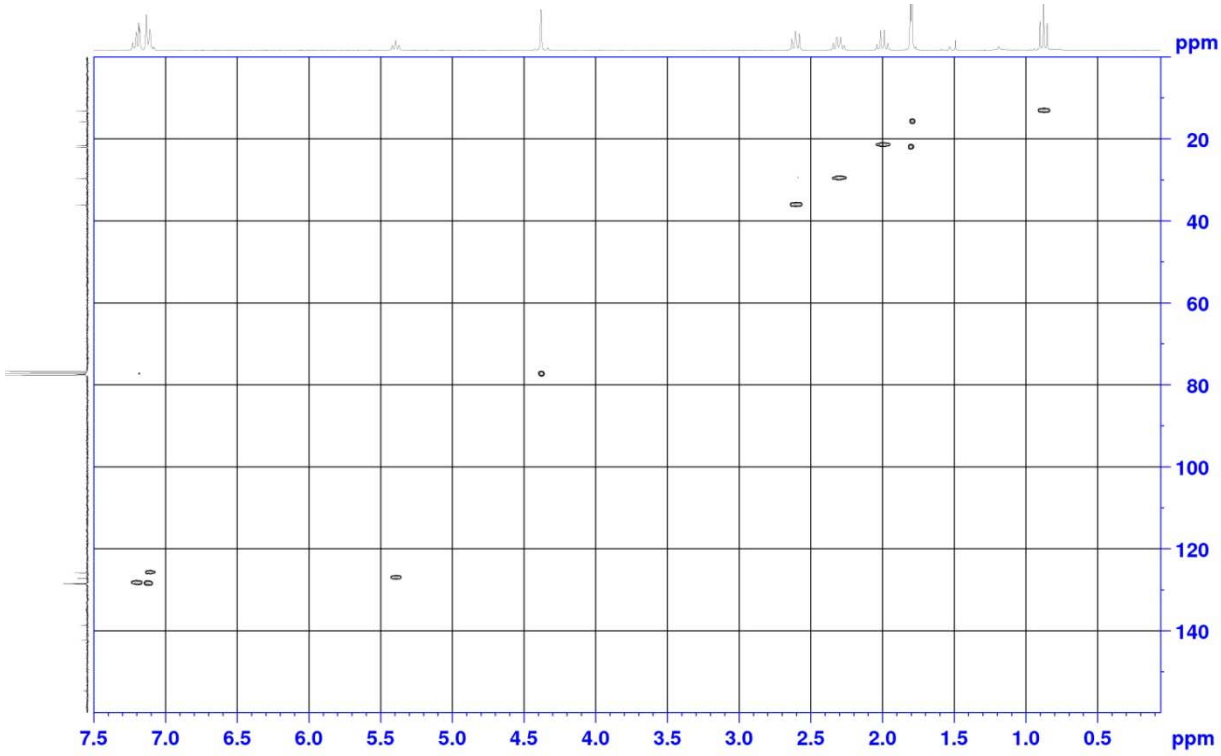
^{13}C NMR



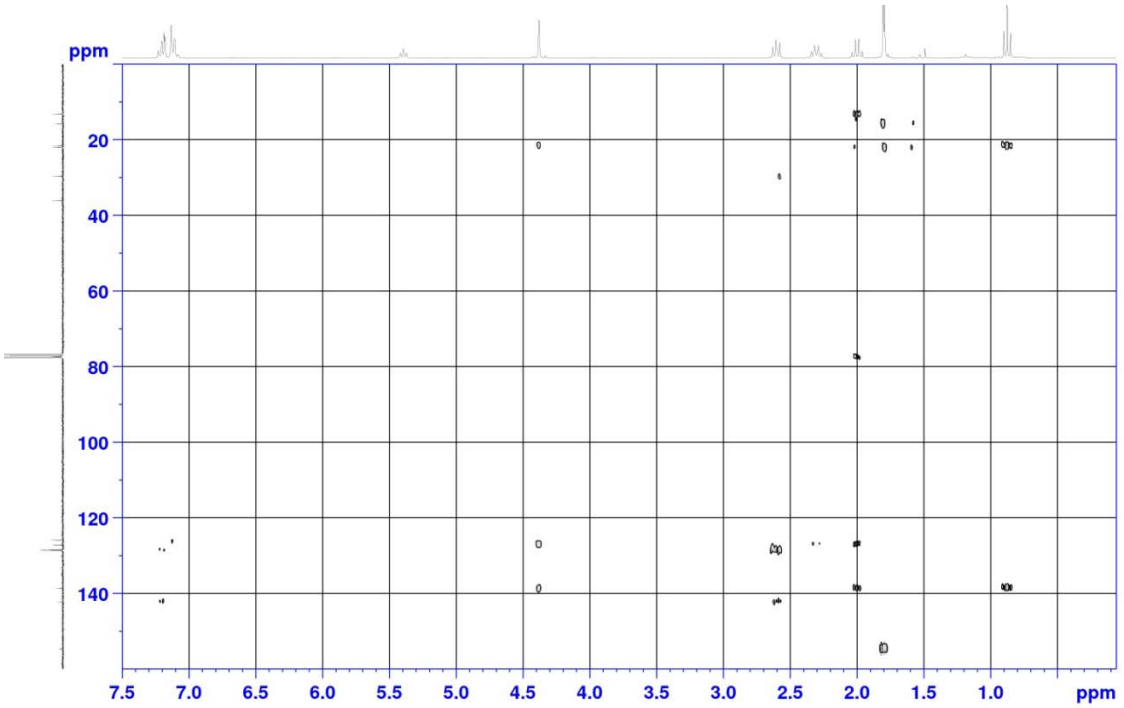


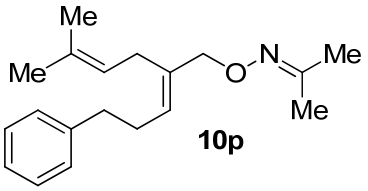
10o

^{1}H-^{13}C HSQC NMR



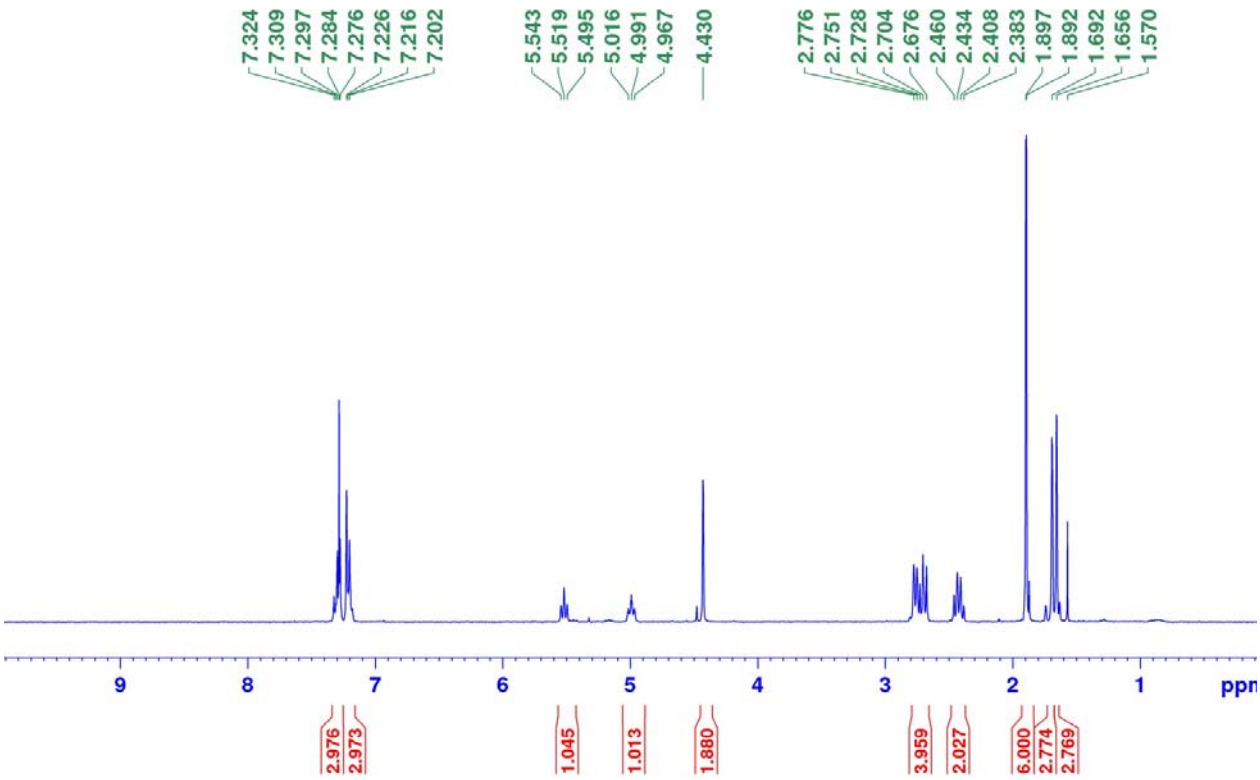
^{1}H-^{13}C HMBC NMR



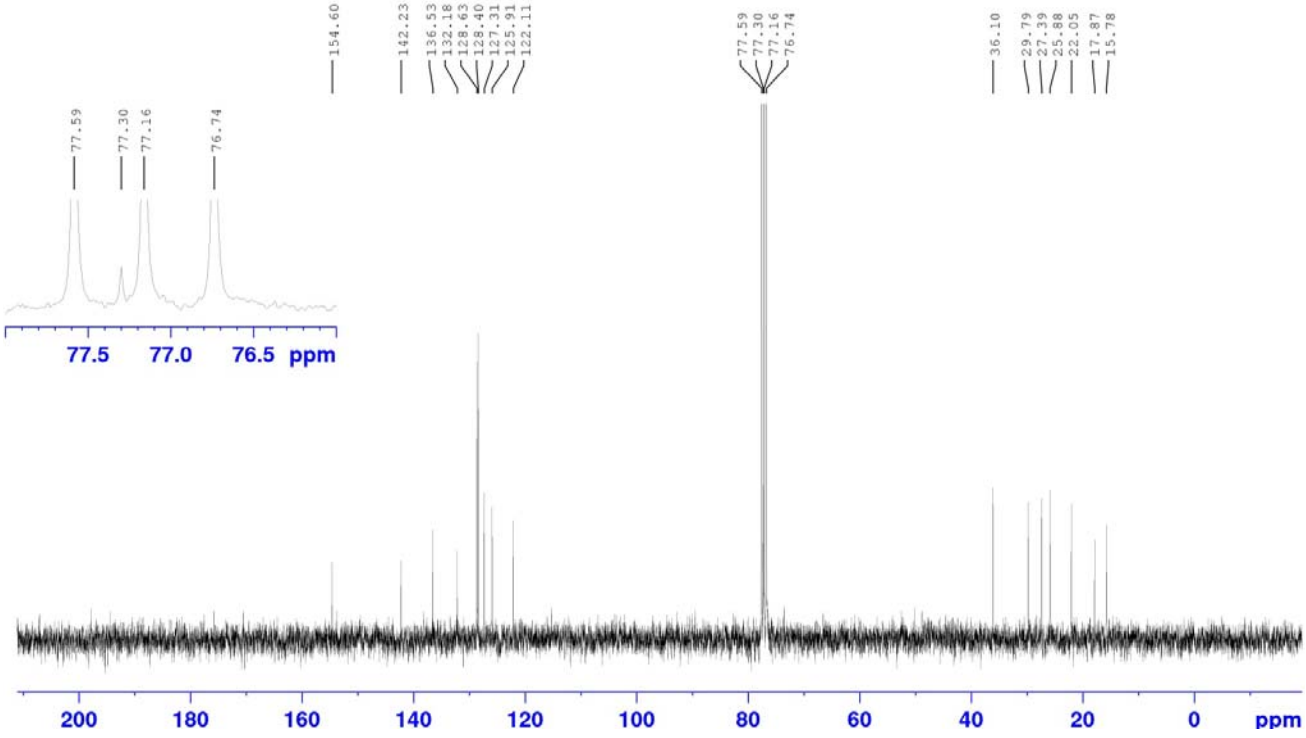


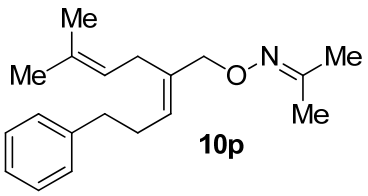
10p

^{1}H NMR



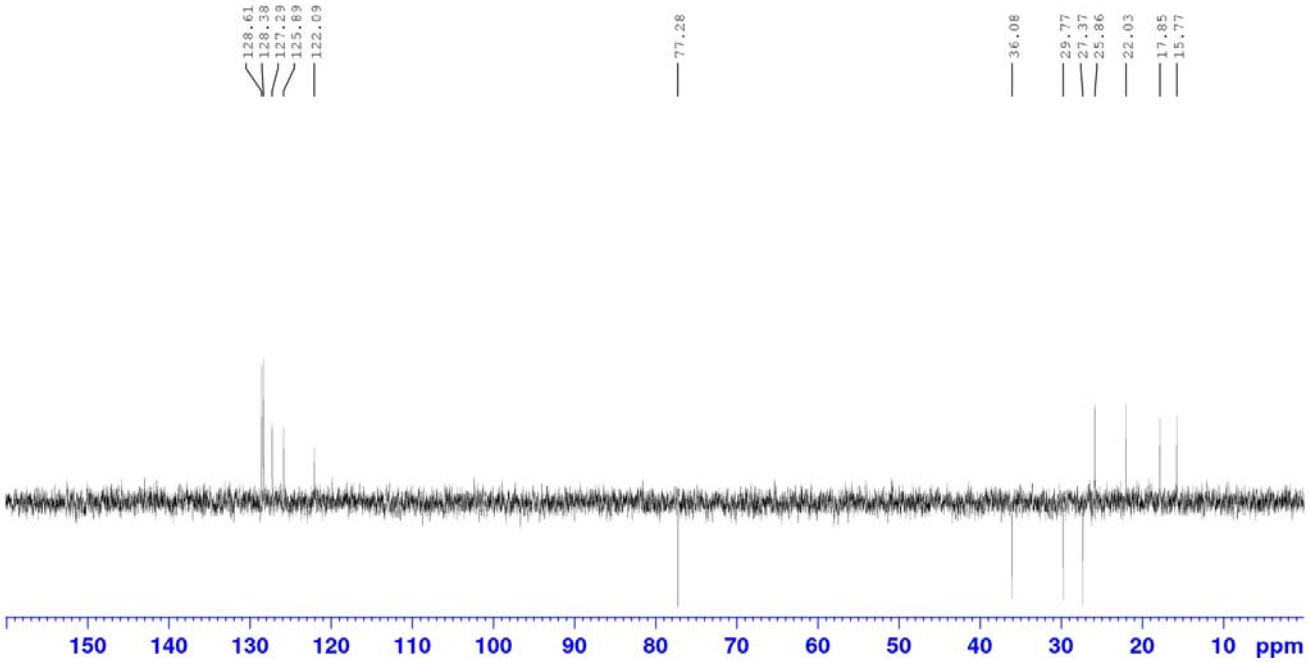
^{13}C NMR



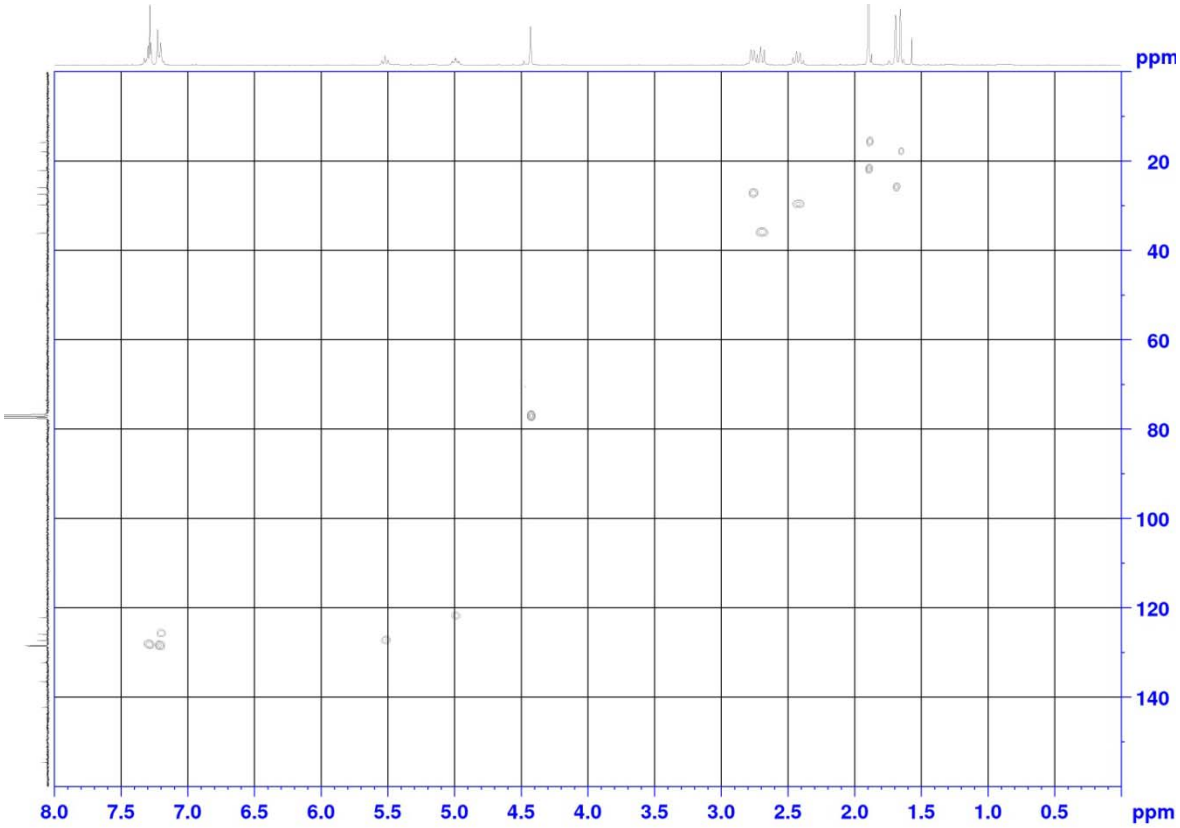


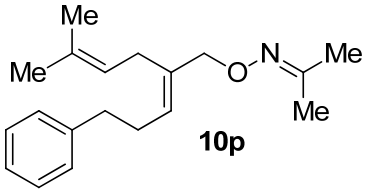
10p

^{13}C DEPT 135 NMR



^{1}H-^{13}C HSQC NMR





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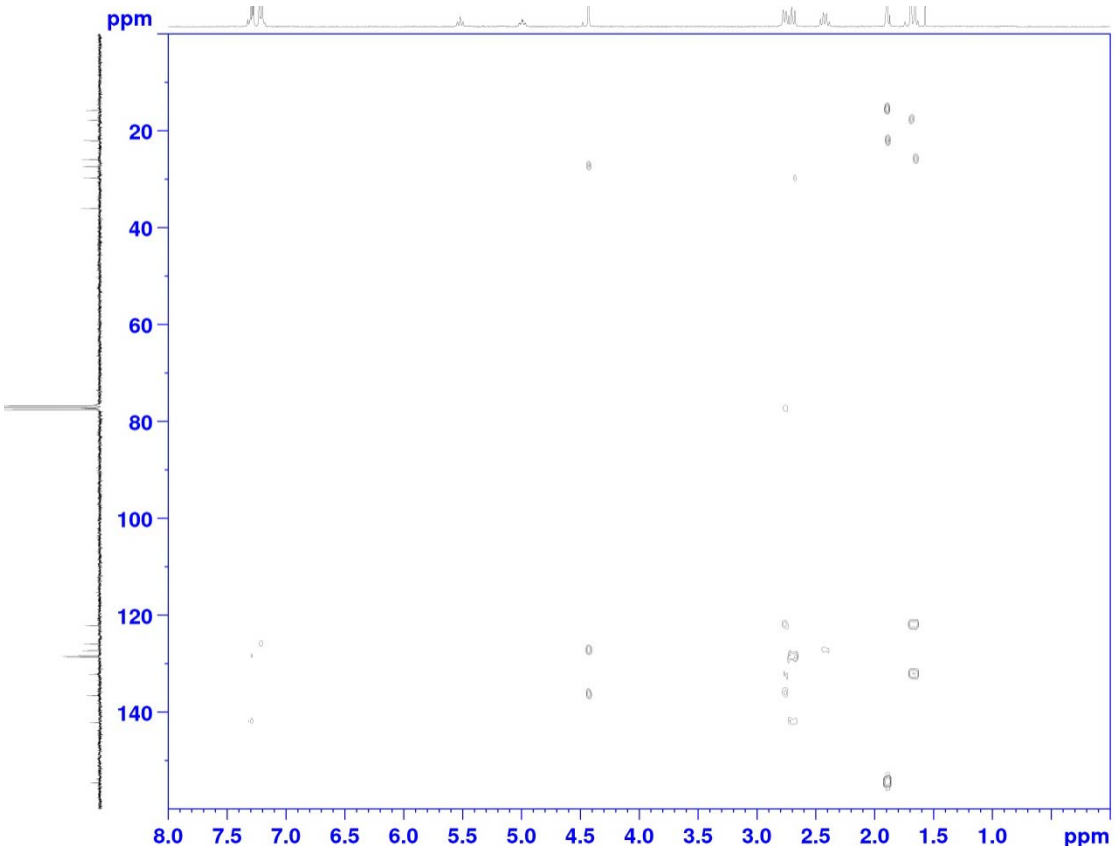
^{1}H-^{13}C HMBC NMR



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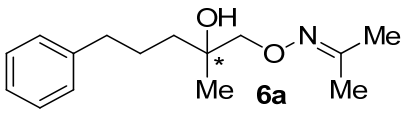

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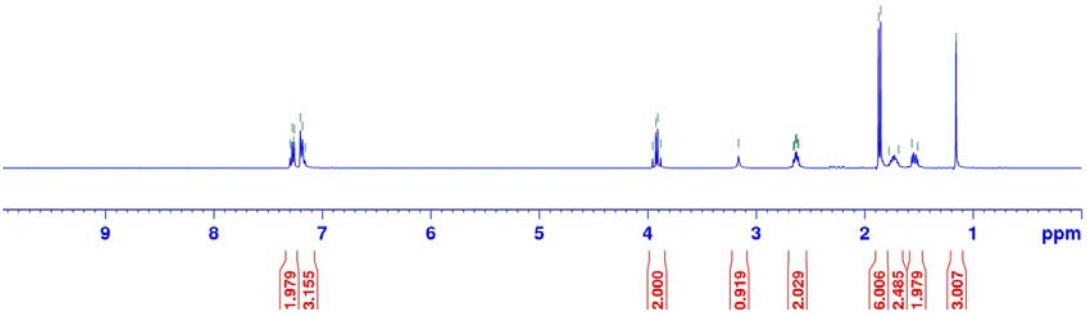

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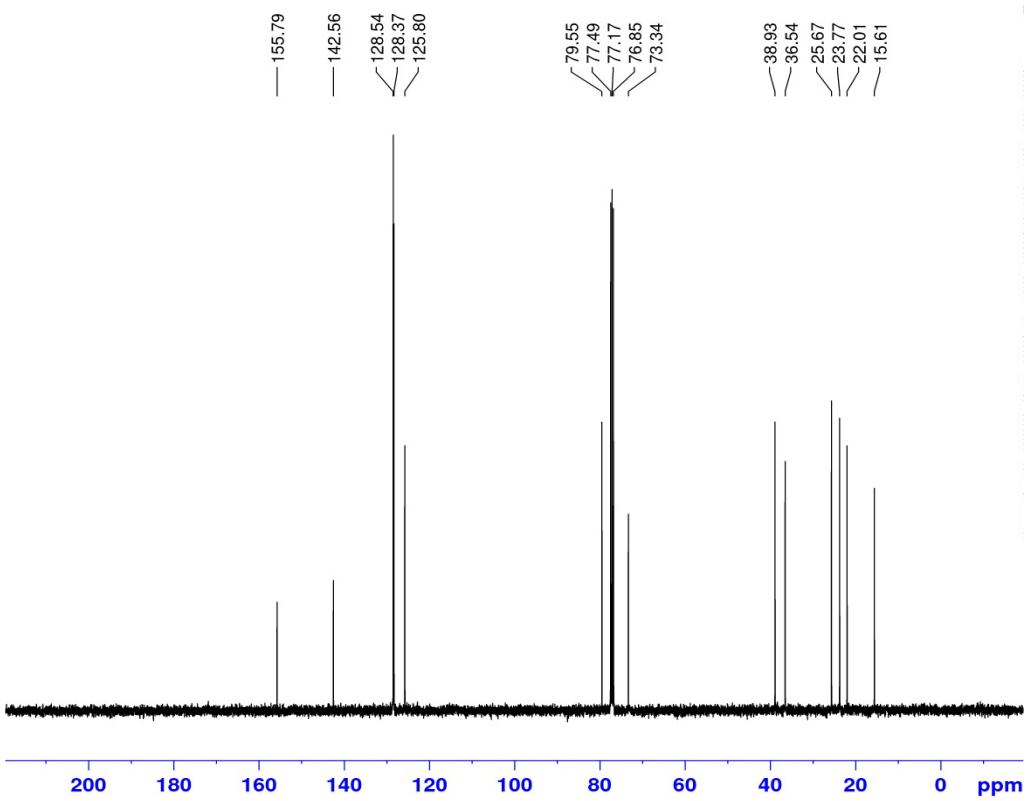
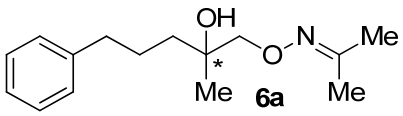


^{13}C DEPT135 NMR



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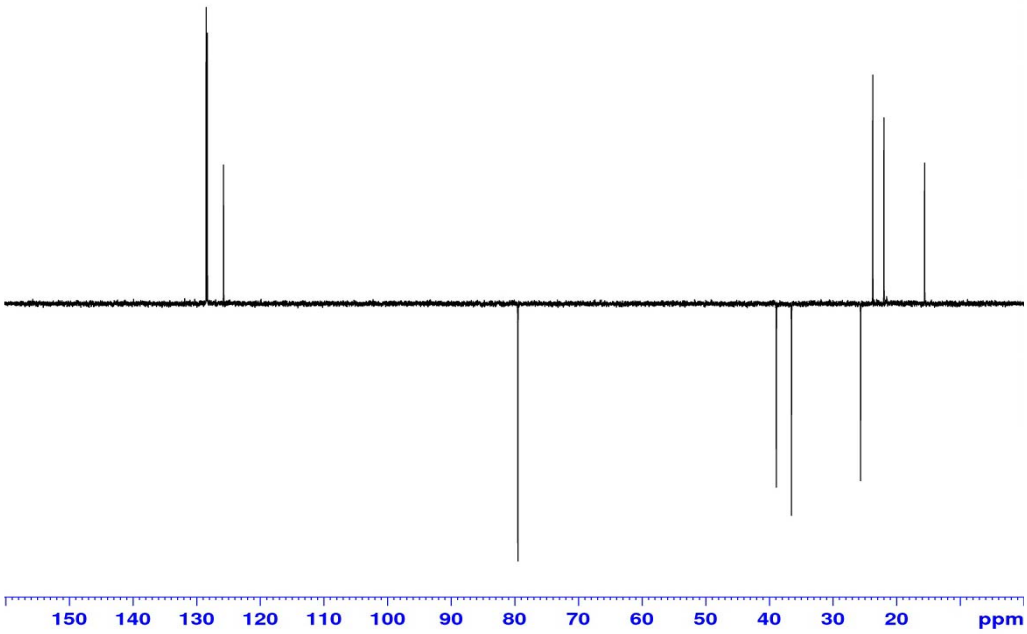

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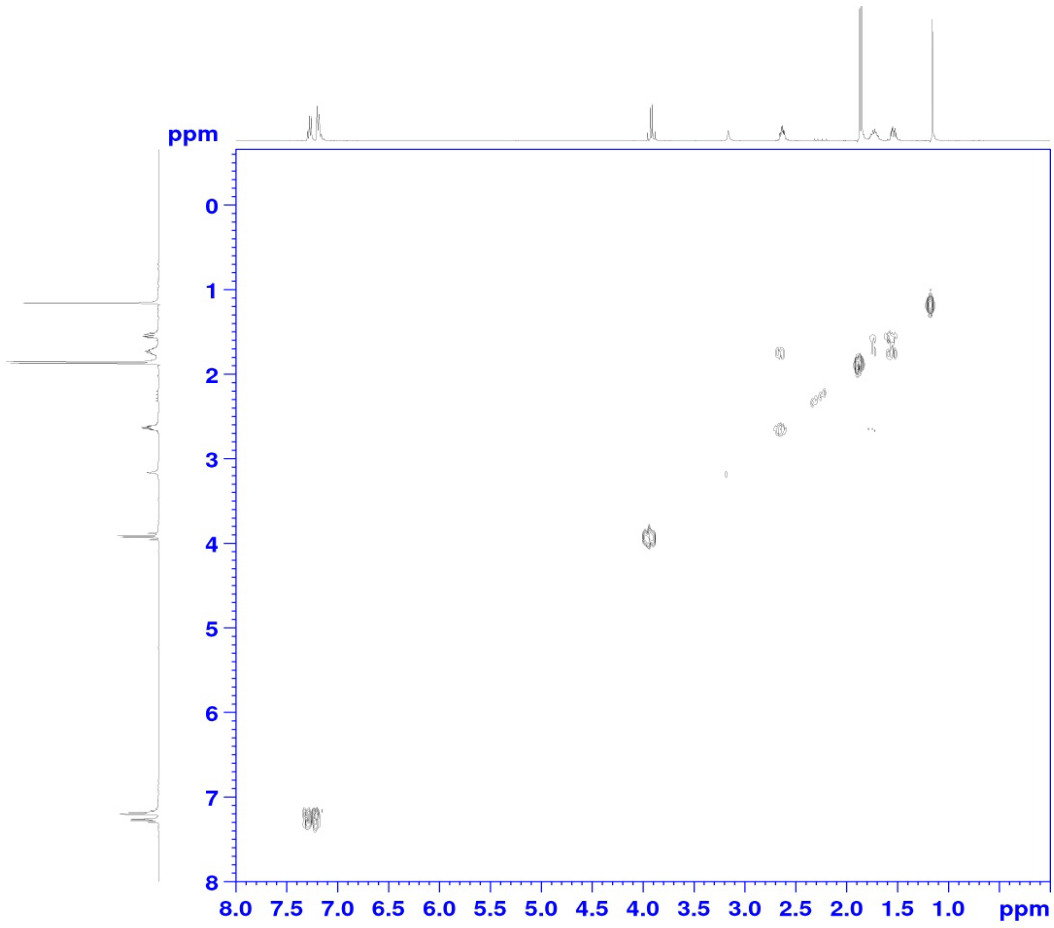
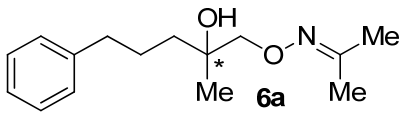
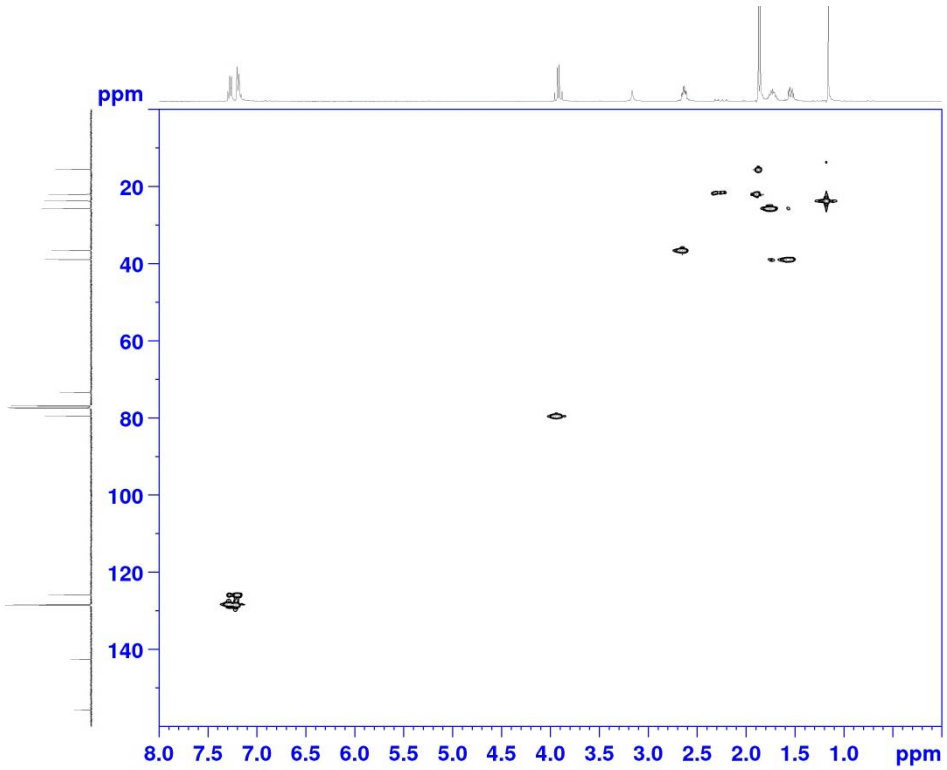


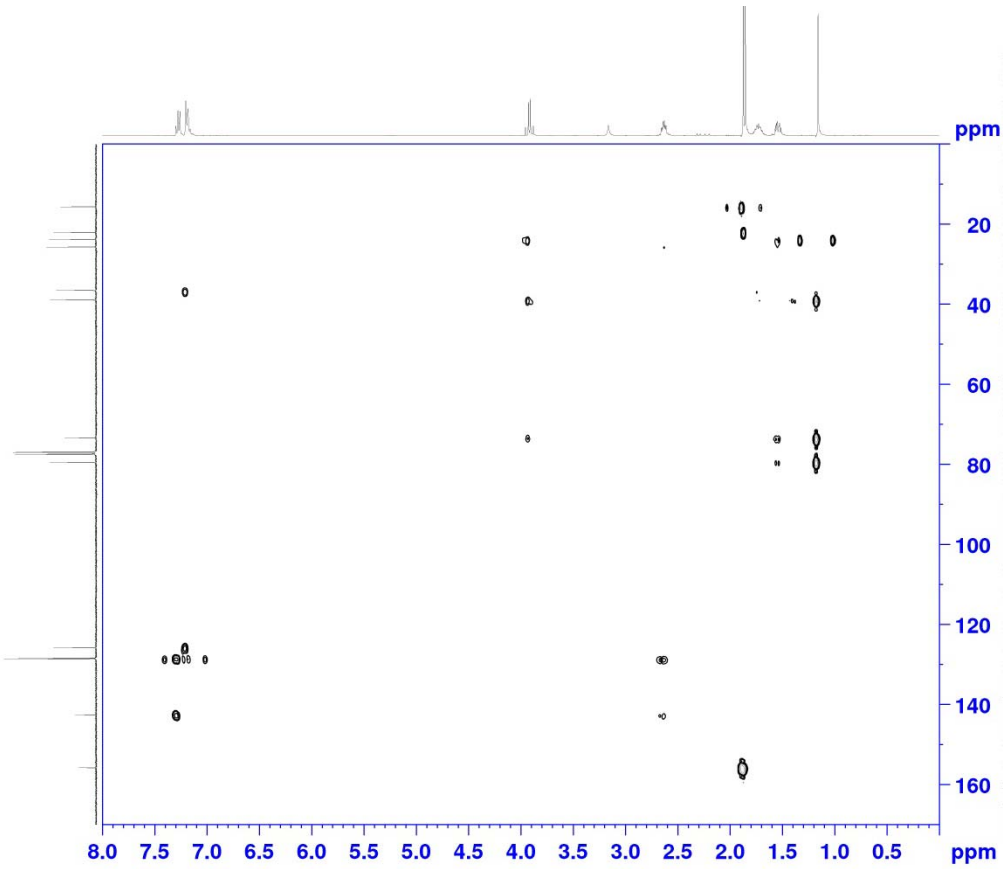
^{1}H-^{13}C HSQC

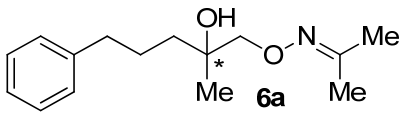


6a



^{1}H-^{13}C HMBC

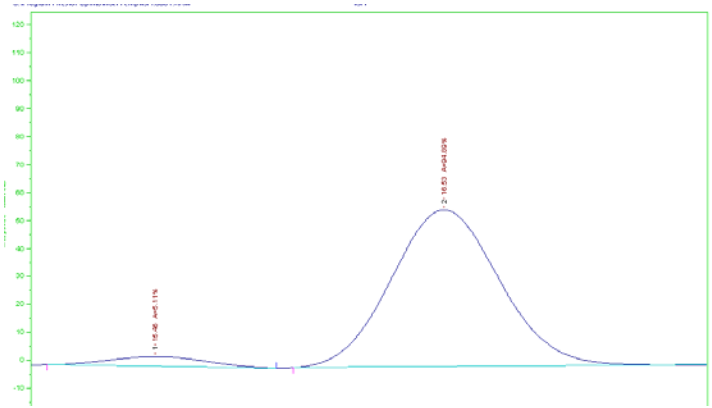




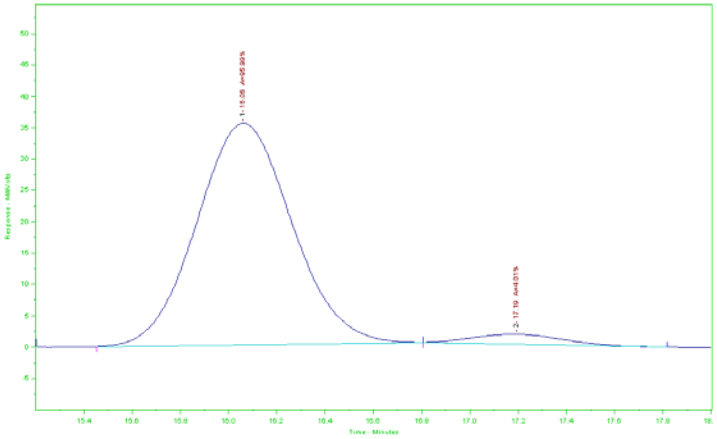
6a

HPLC traces (Chiralpak-IB, 97:3 hexanes/isopropanol@ 1.0 mL/min)

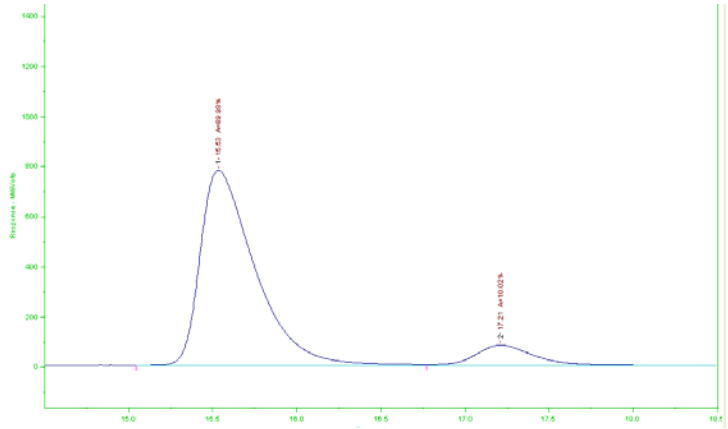
a) *S:R* = 5:95; after CAHB of **5a** with (*R*,*R*)-**L**

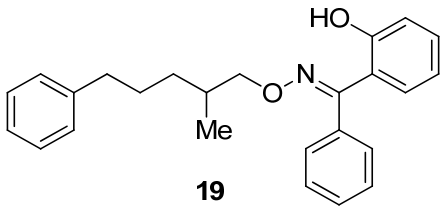


b) *S:R* = 96:4 after CAHB of (*E*)-**10a** with (*R*,*R*)-L



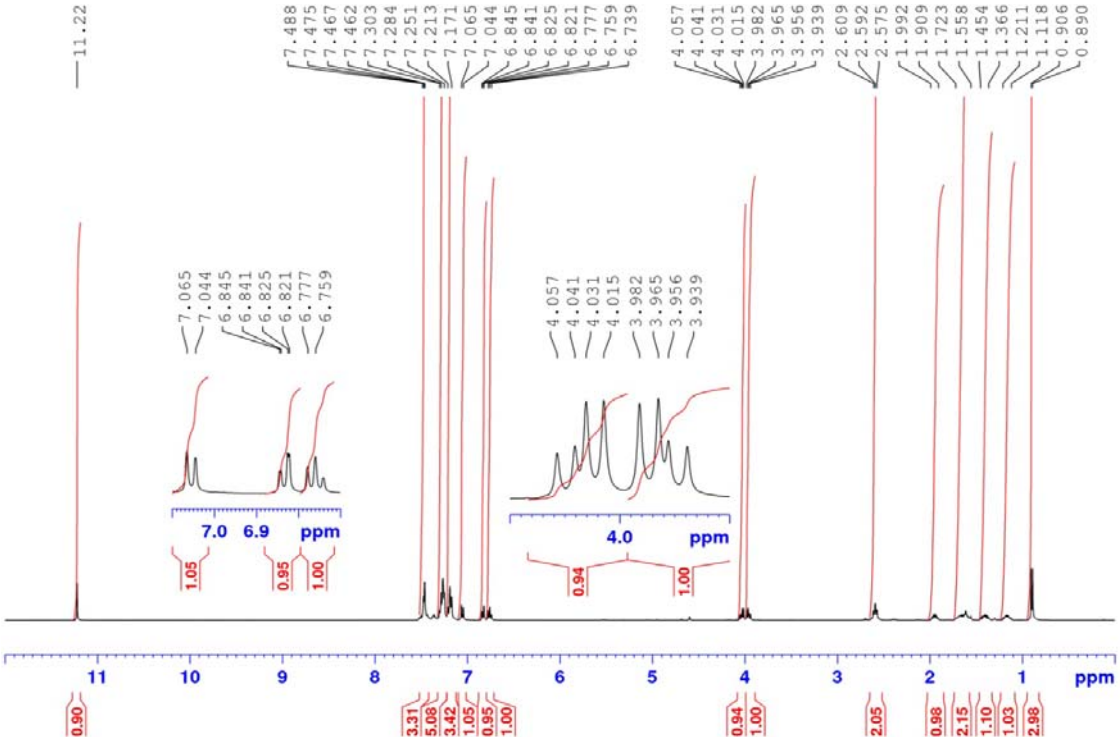
c) *S:R* = 90:10 after CAHB of *(Z)*-**10a** with (*R*,*R*)-L



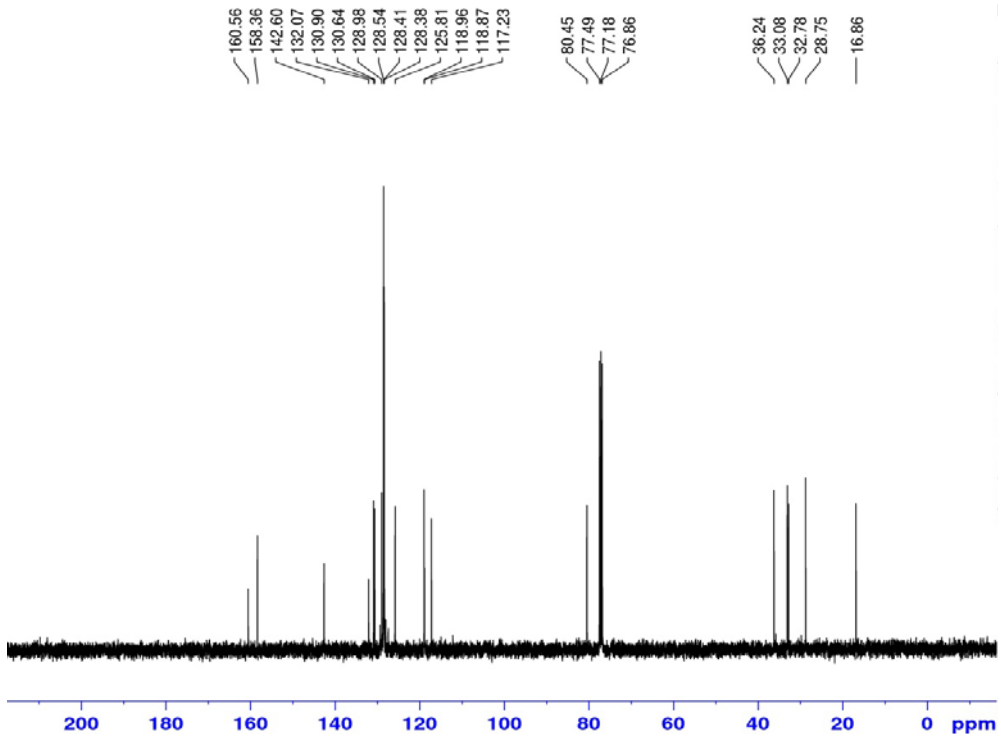


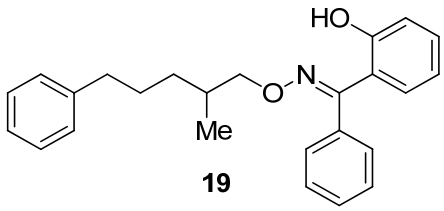
19

^{1}H NMR



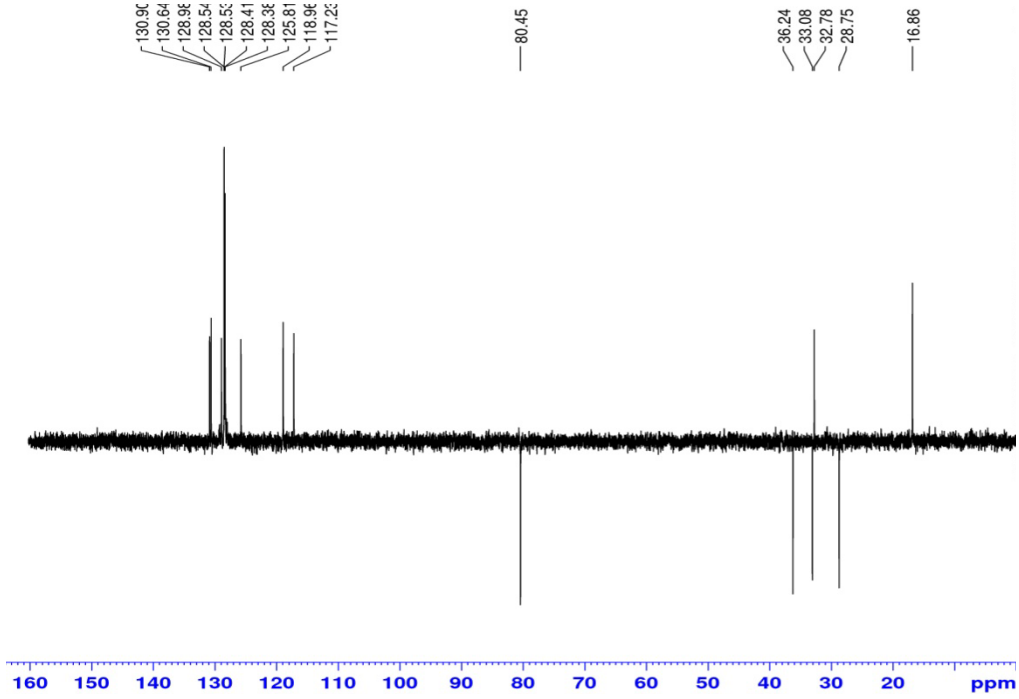
^{13}C NMR



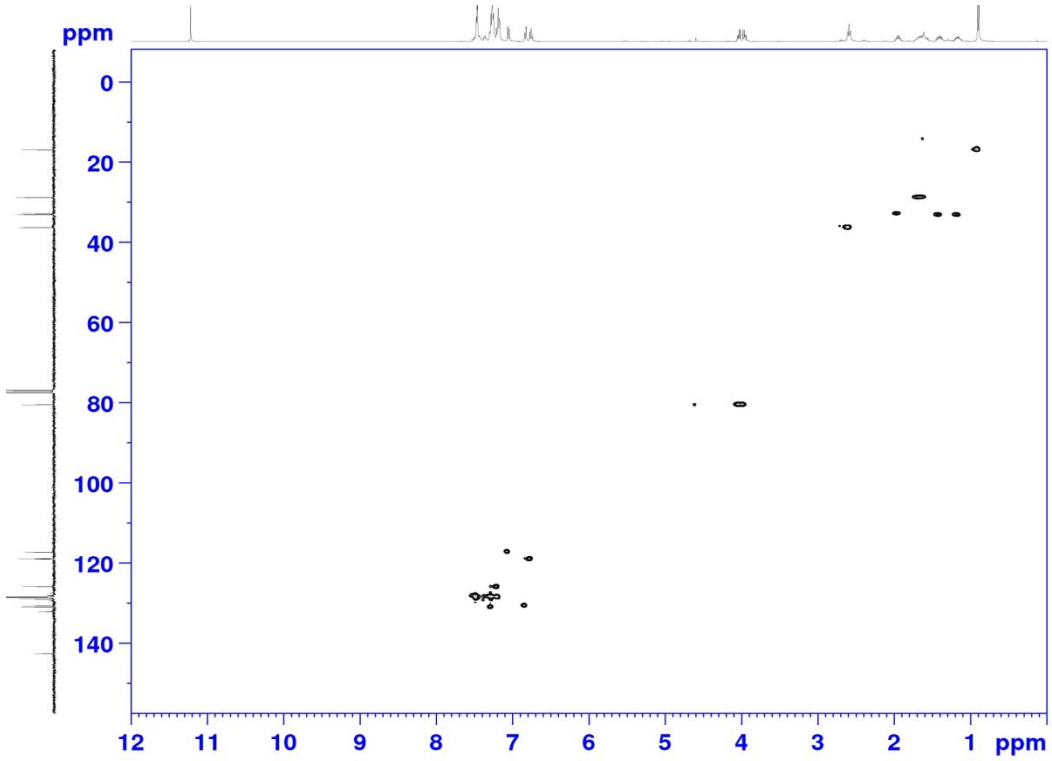


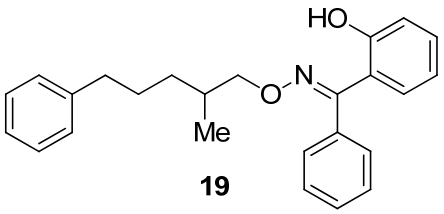
19

^{13}C DEPT 135 NMR



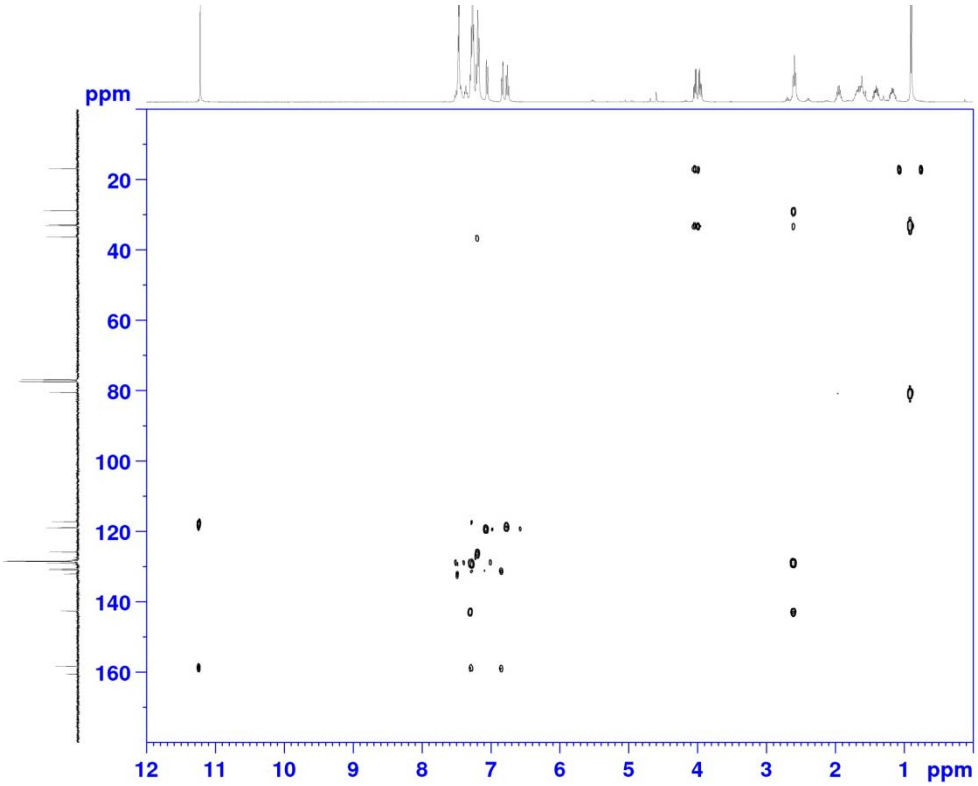
^{1}H-^{13}C HSQC NMR

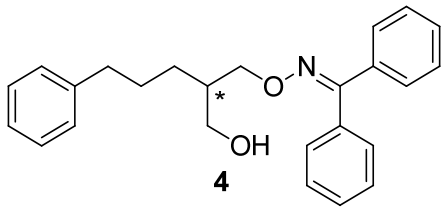




19

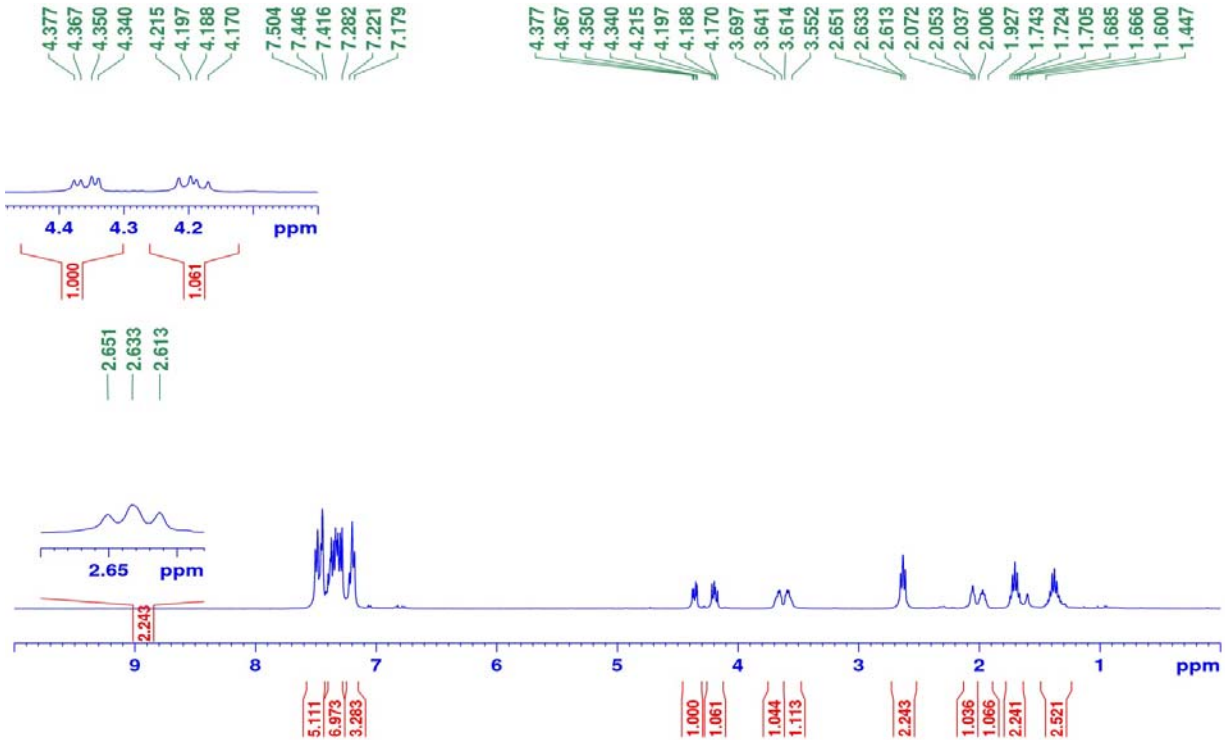
^{1}H-^{13}C HMBC NMR



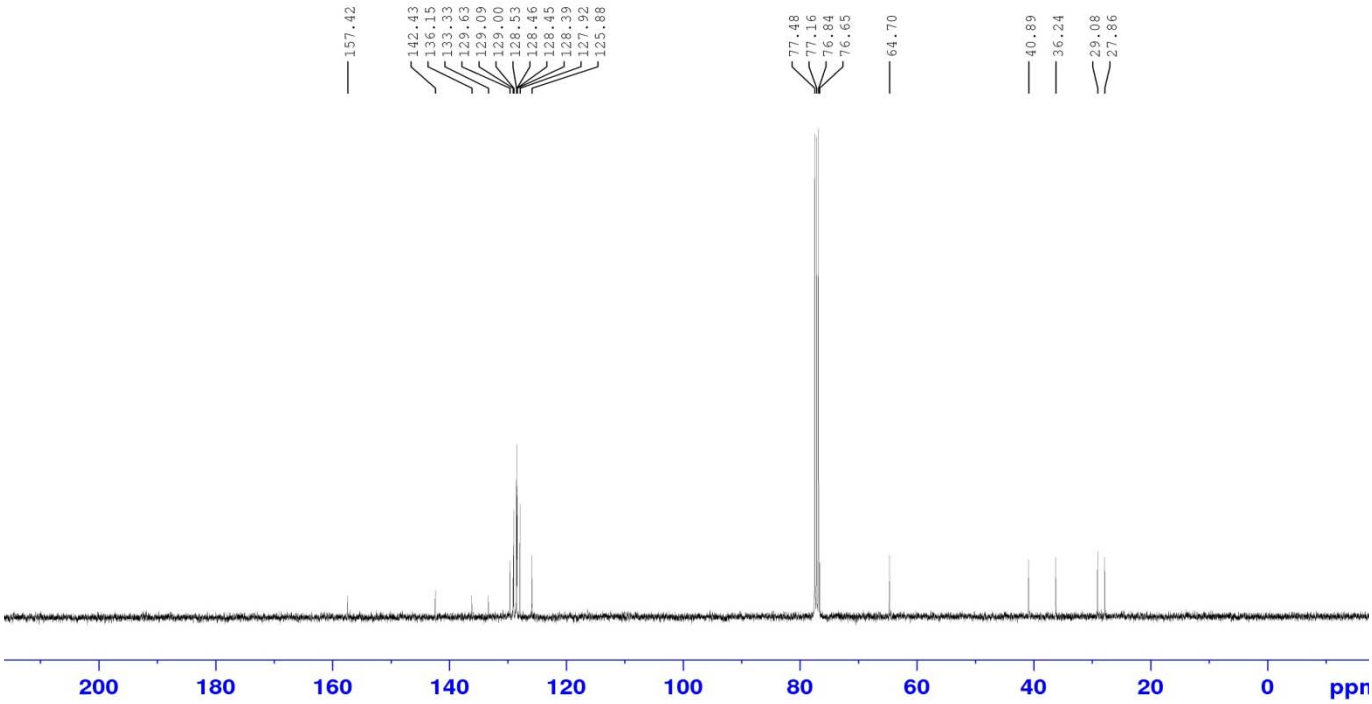


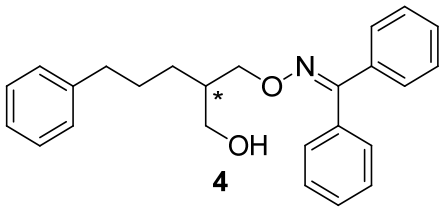
4

^{1}H NMR



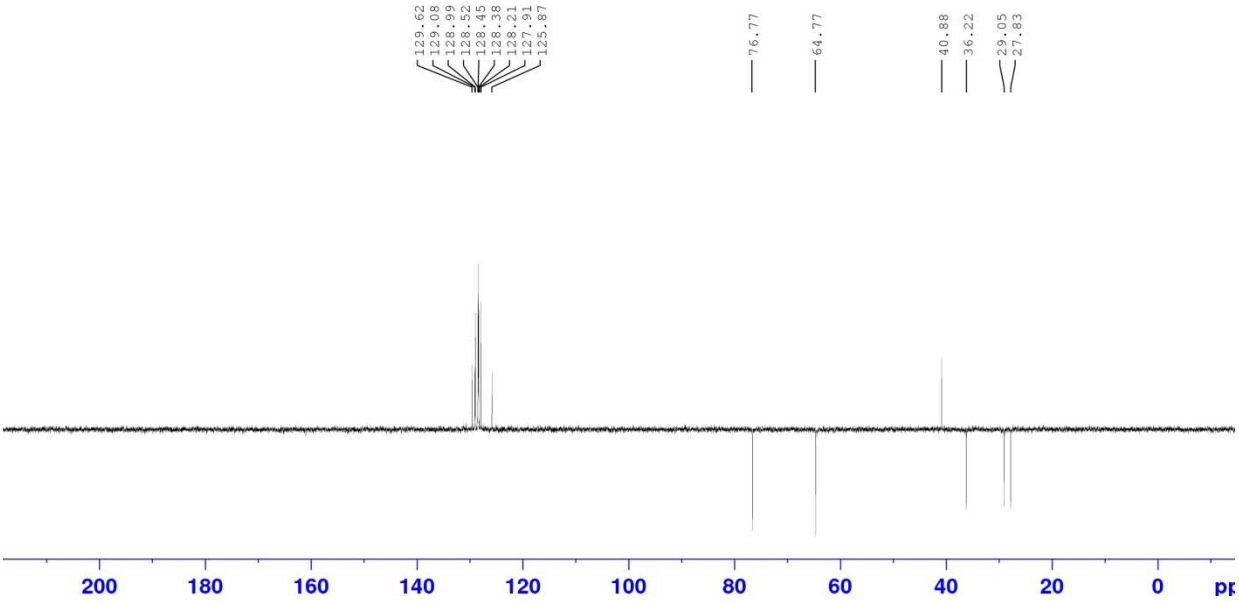
^{13}C NMR



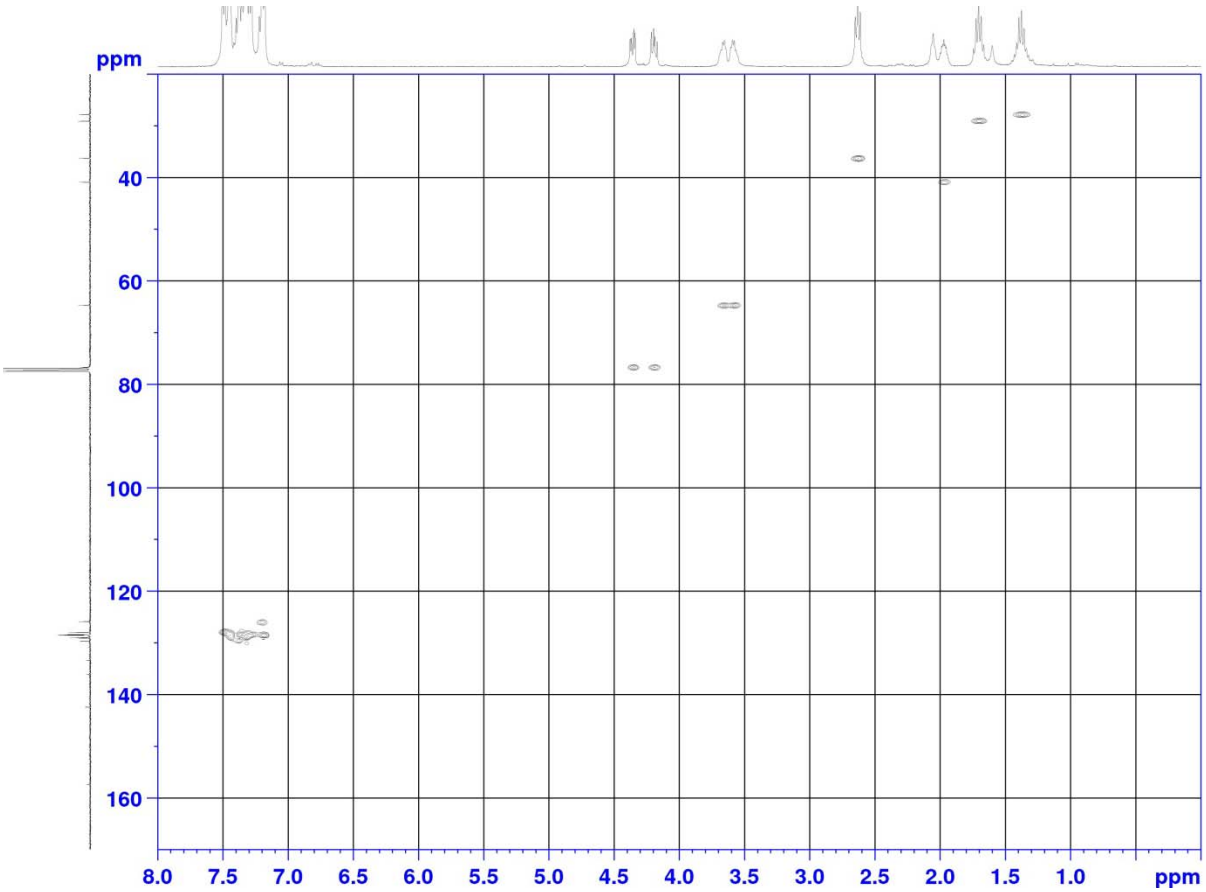


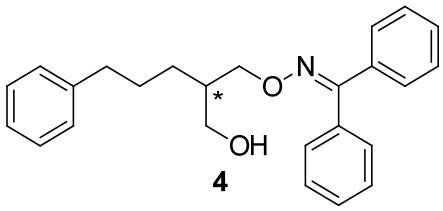
4

^{13}C DEPT 135 NMR



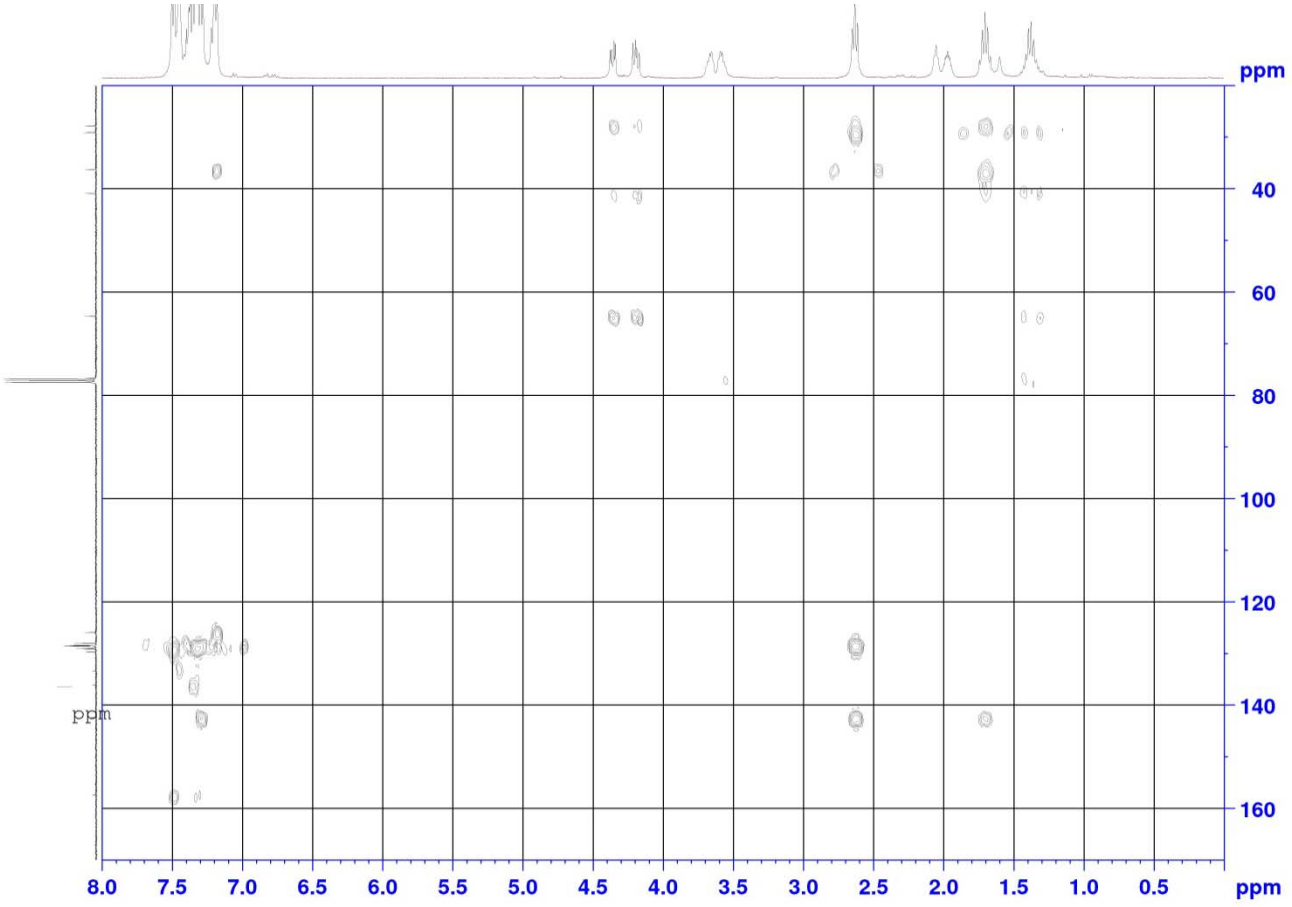
^{1}H-^{13}C HSQC





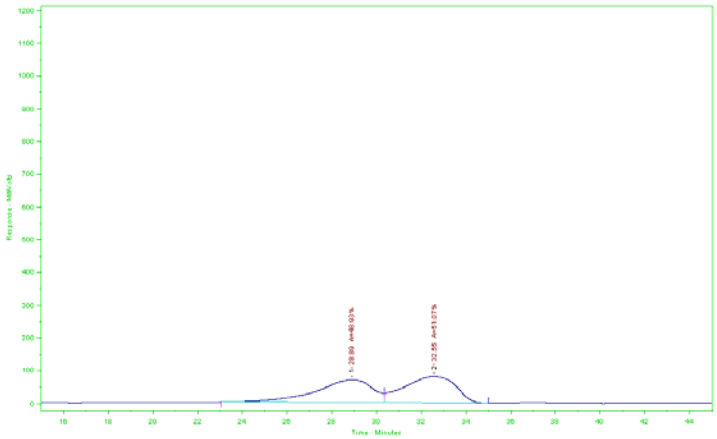
4

^{1}H-^{13}C HMBC NMR

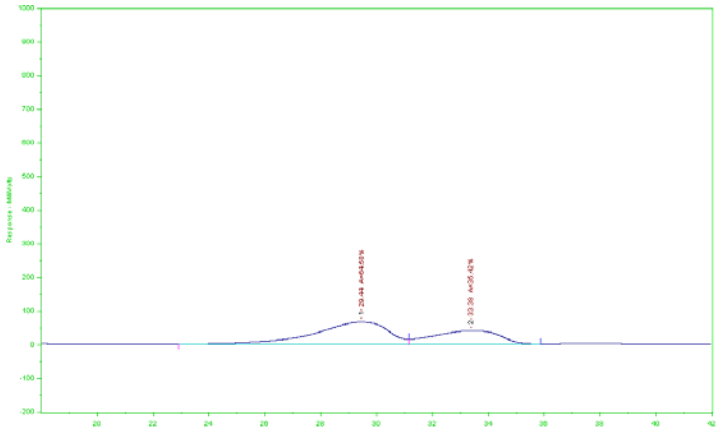


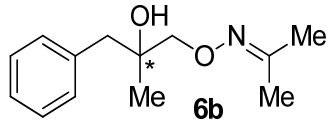
HPLC traces (Chiralpak-IC, 95:5 hexanes/isopropanol@ 1.5 mL/min)

a) racemic mixture



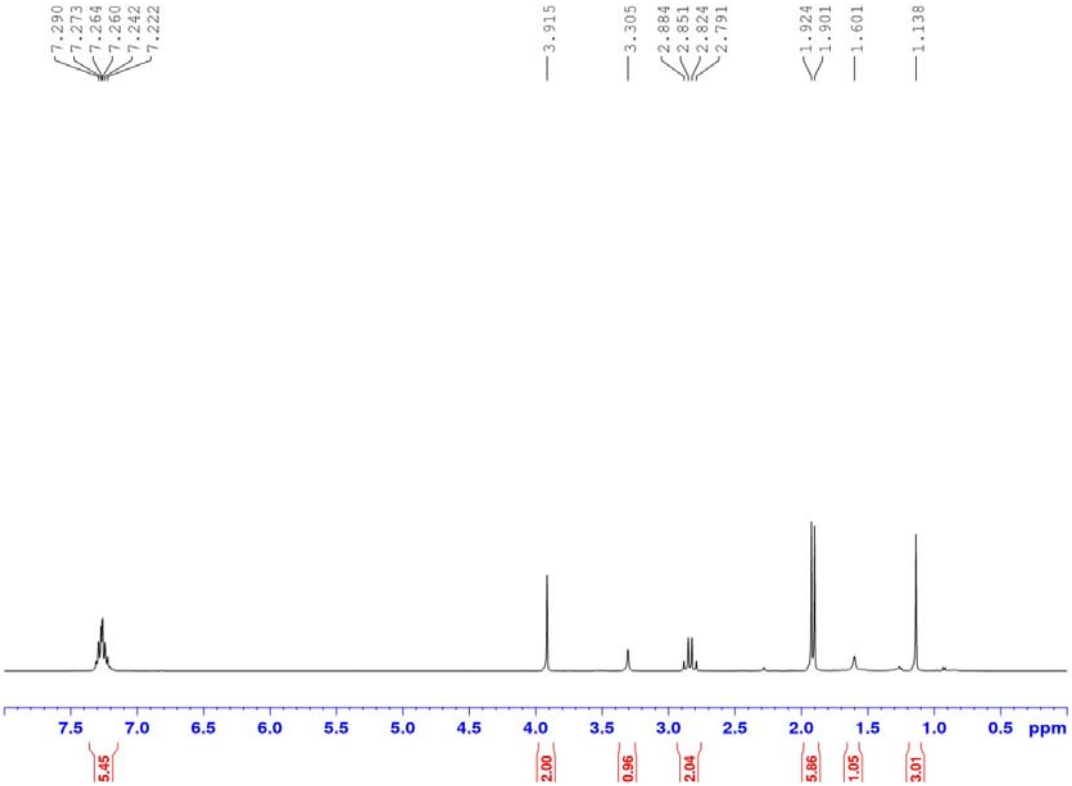
b) after CAHB of **3** with (*S*,*S*)-**L**



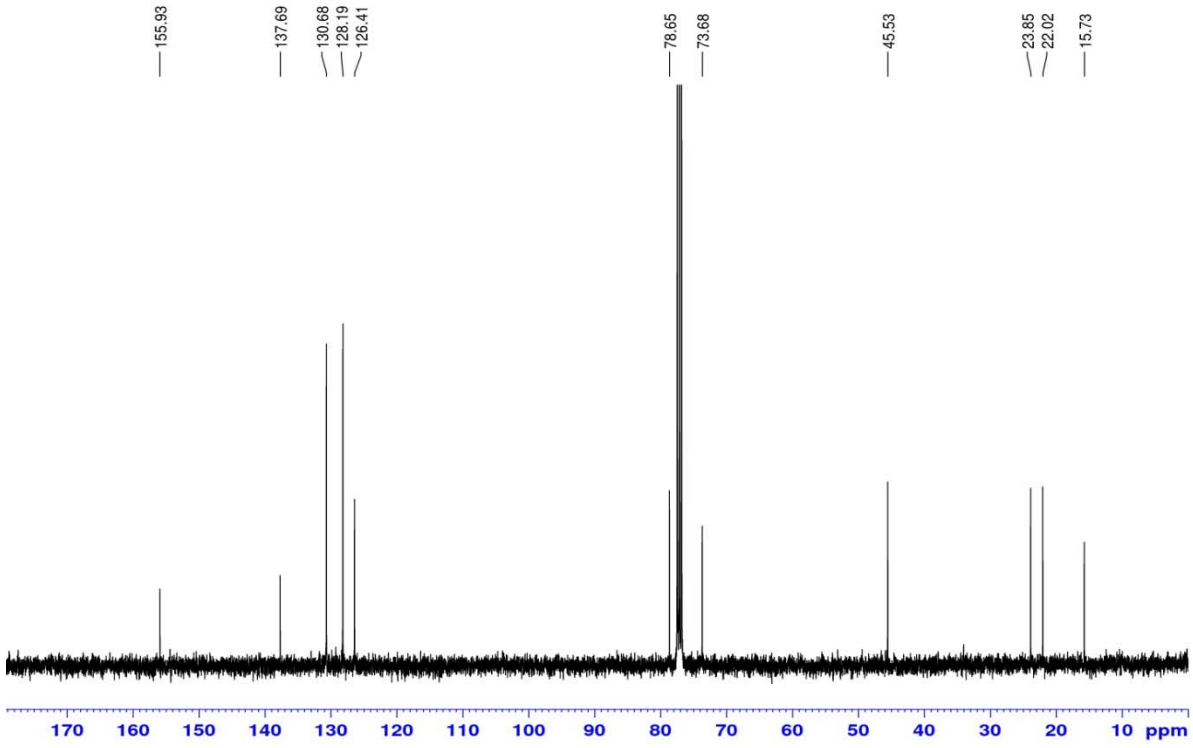


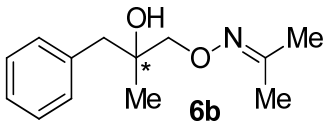
6b

^{1}H NMR



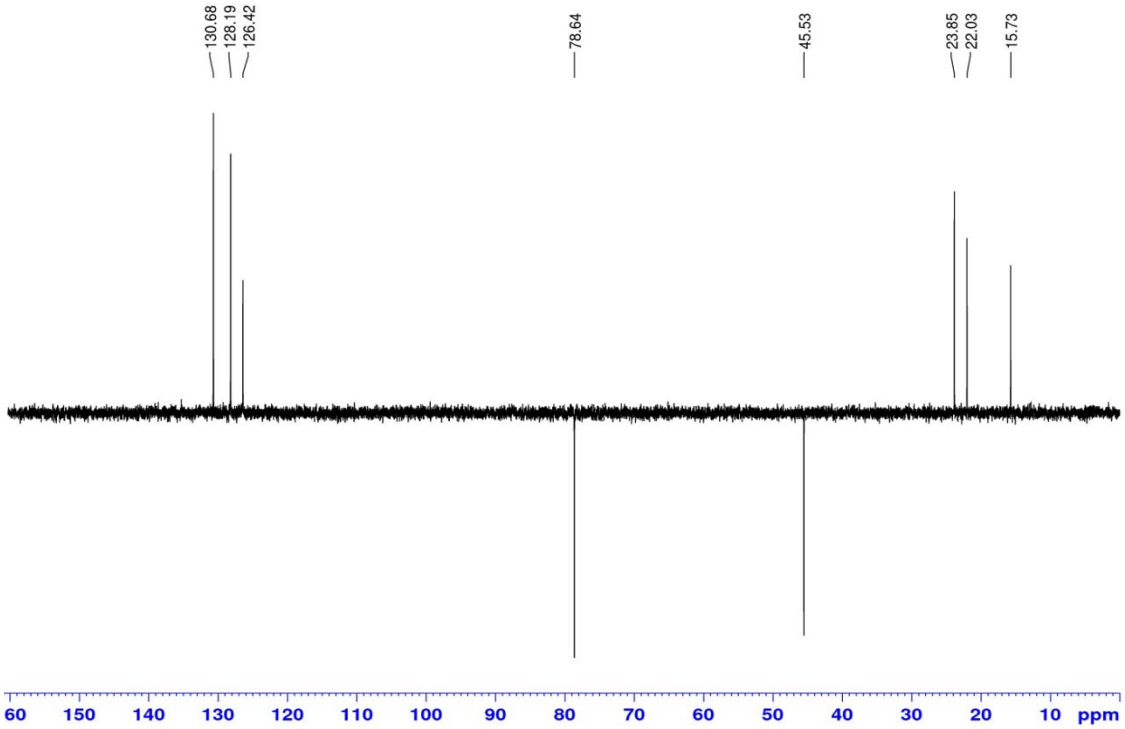
^{13}C NMR



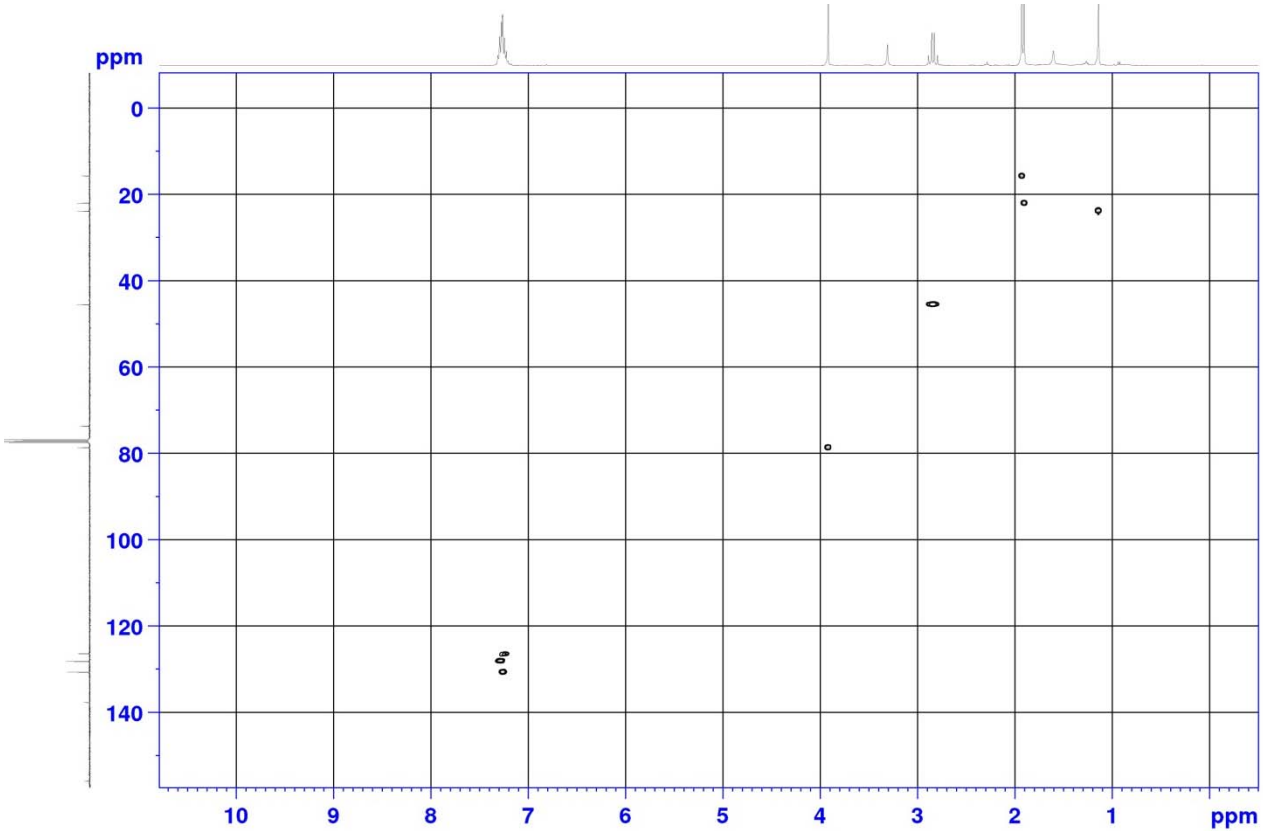


6b

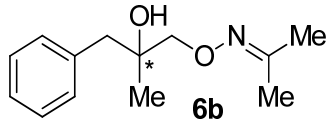
^{13}C DEPT 135 NMR



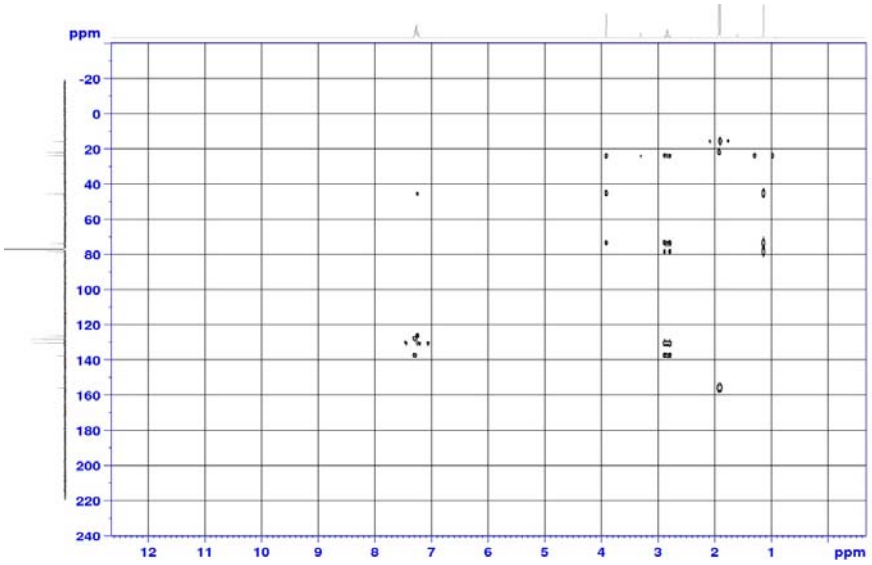
^{1}H- ^{13}C HSQC NMR



^{1}H- ^{13}C HMBC NMR

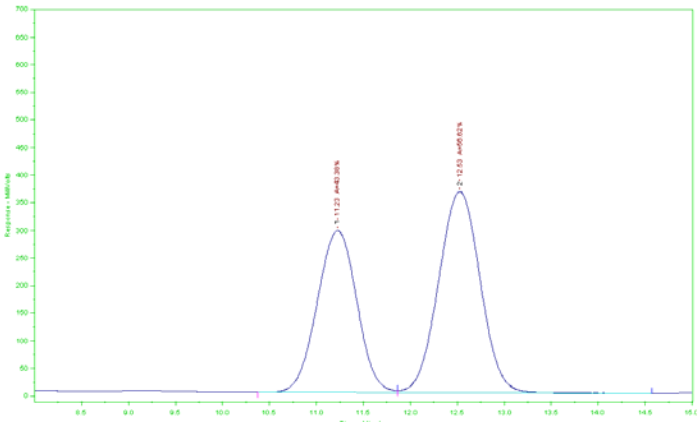


6b

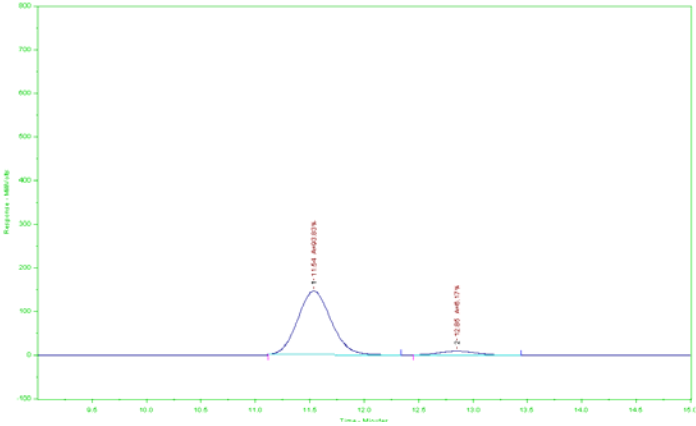


HPLC traces (Chiralpak-AD, 90: 10 hexanes/isopropanol @ 1.0 mL/min)

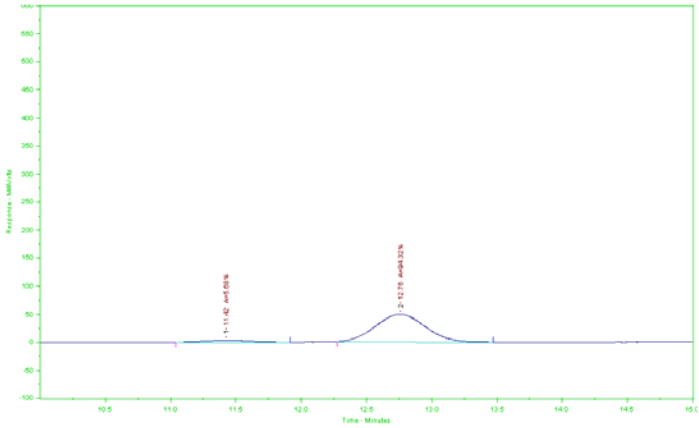
a) racemic mixture



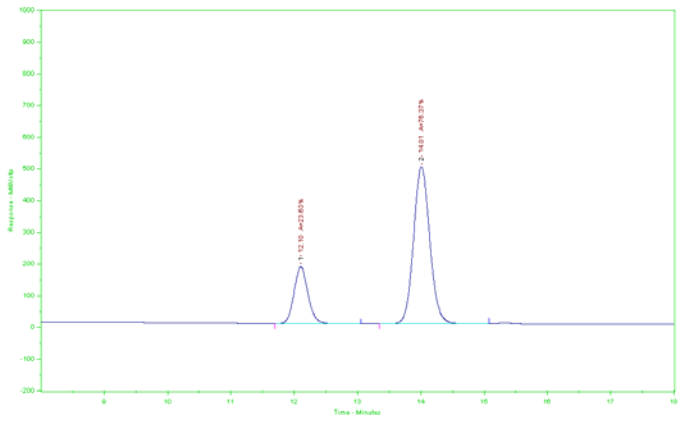
b) *R*:*S* = 94:6 after CAHB of **5b** with (*R*,*R*)-**L**



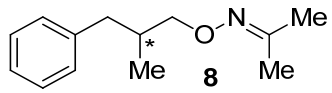
c) *R*:*S* = 6:94 after CAHB of **5b** with (*S*,*S*)-**L**



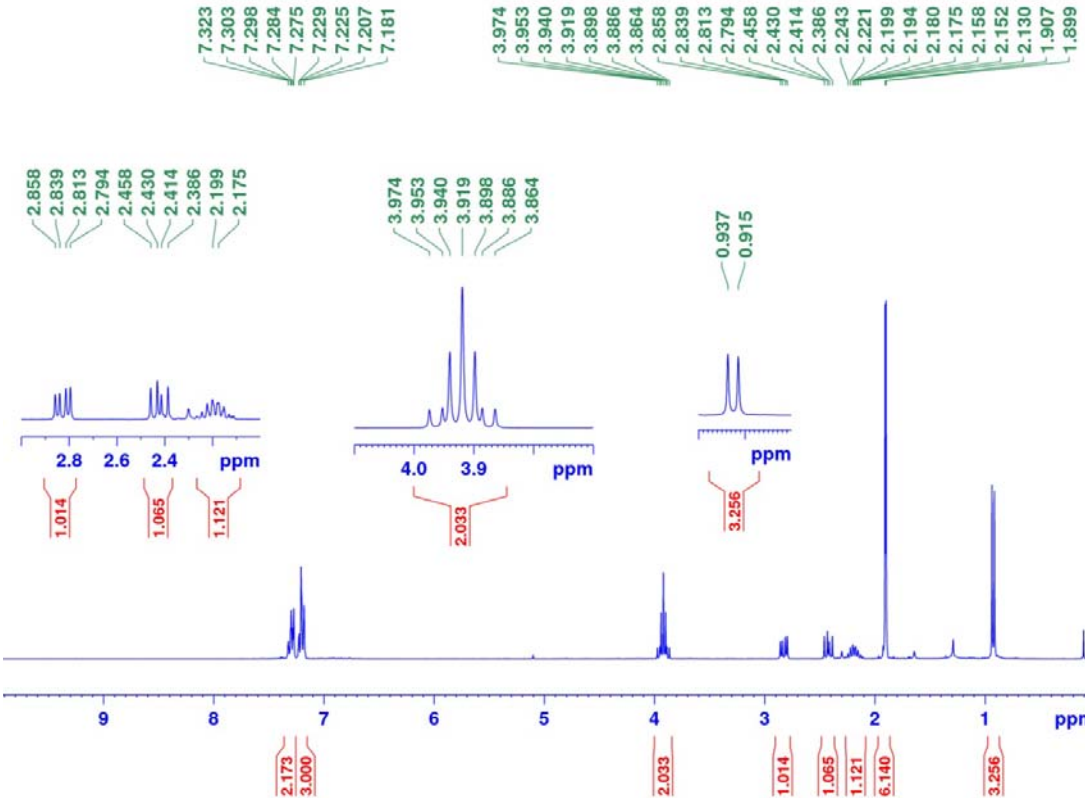
d) *R*:*S* = 24:76 after CAHB of **10b** with (*R*,*R*)-**L**



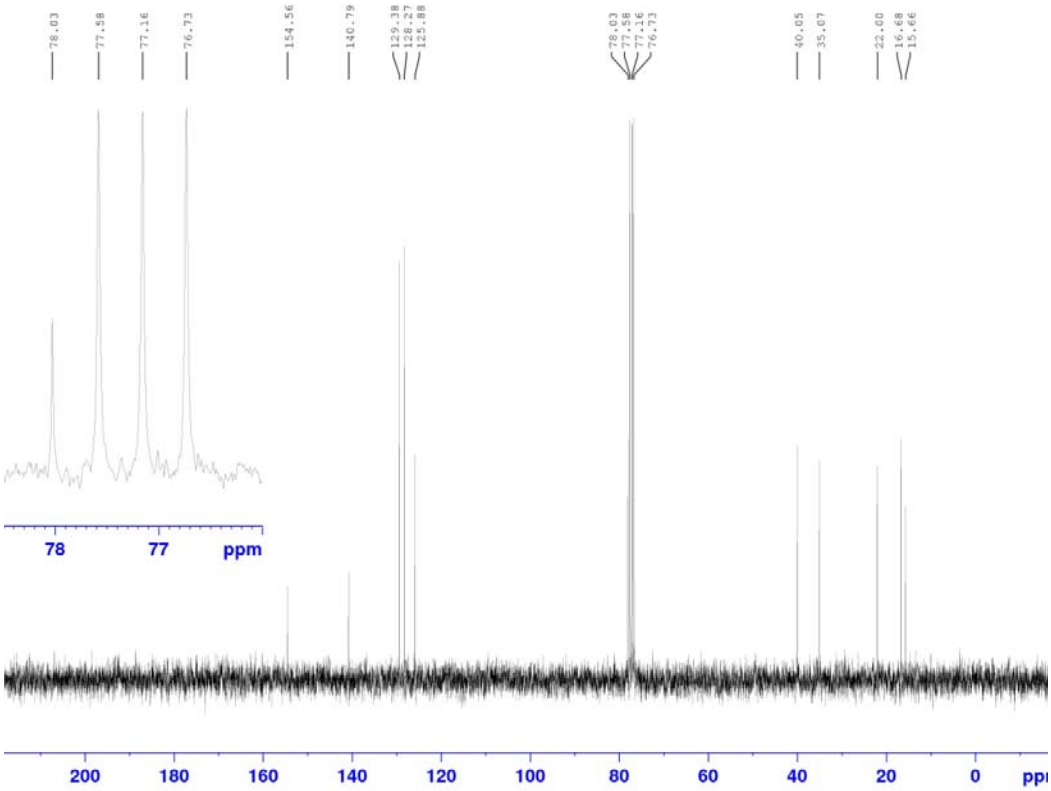
^{1}H NMR



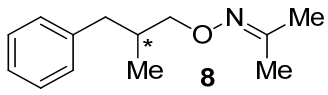
8



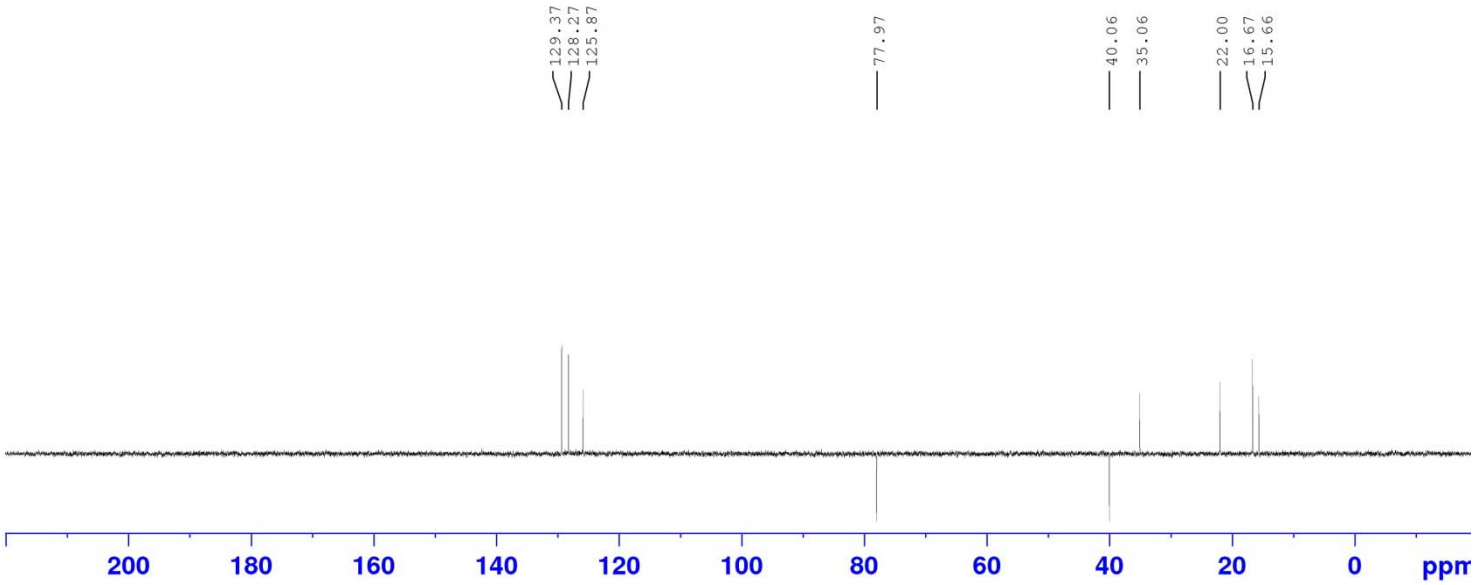
^{13}C NMR



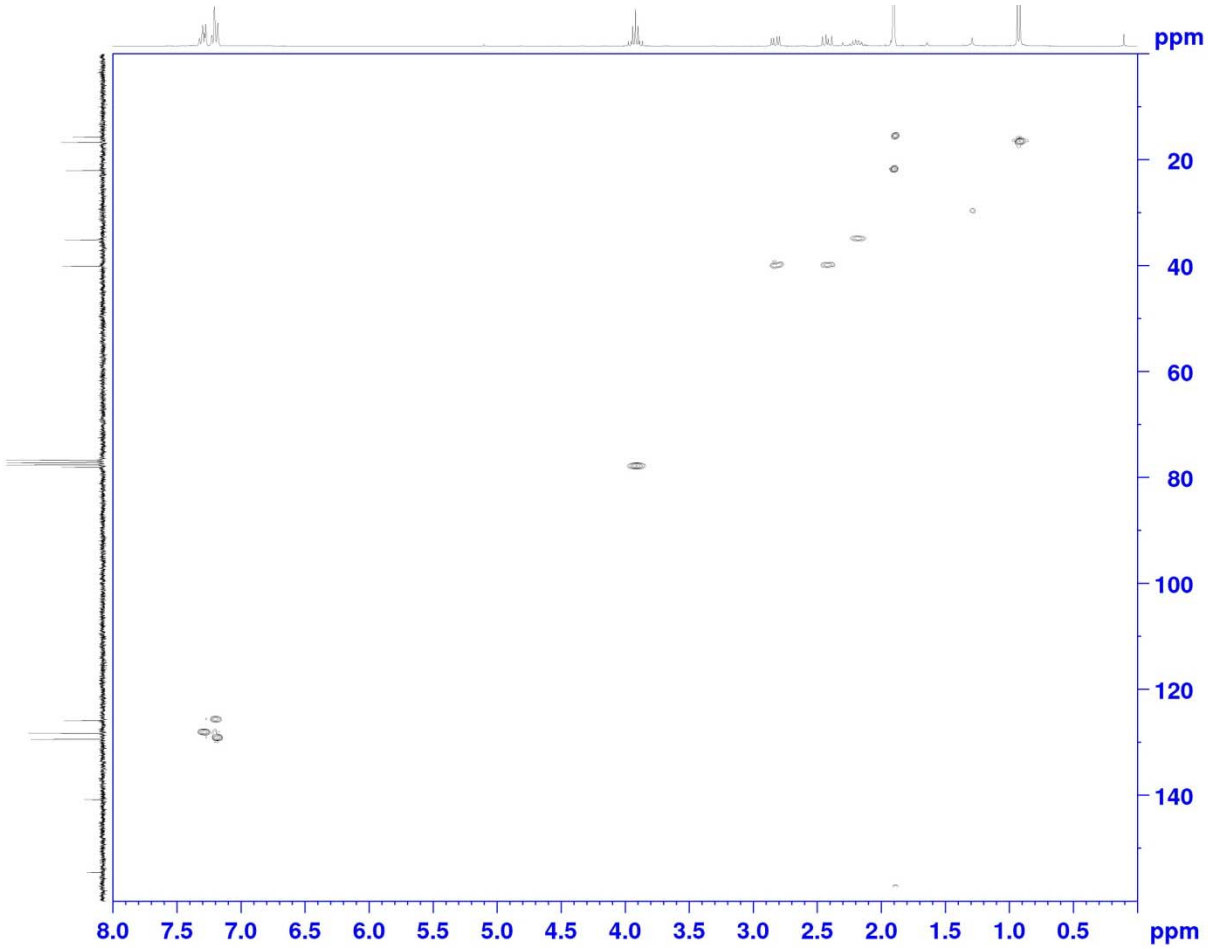
^{13}C DEPT 135 NMR



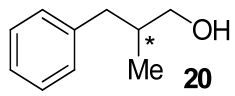
8



^{1}H- ^{13}C HSQC NMR



^{1}H NMR



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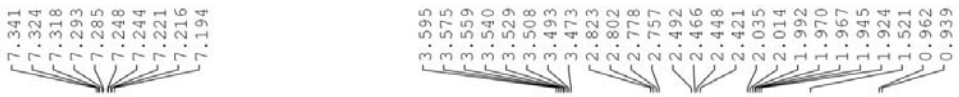
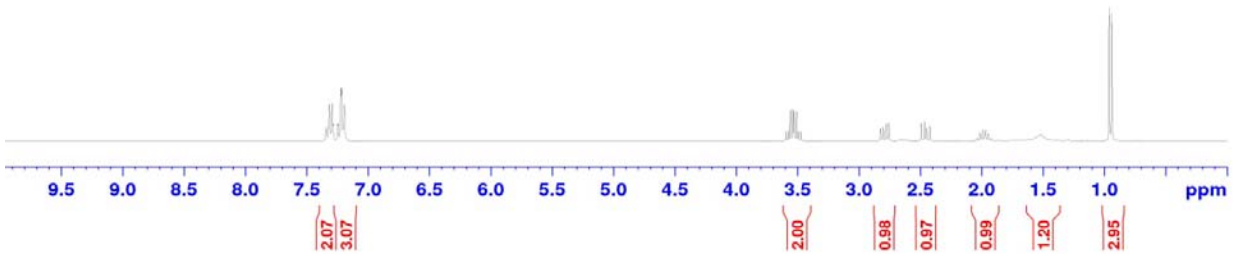
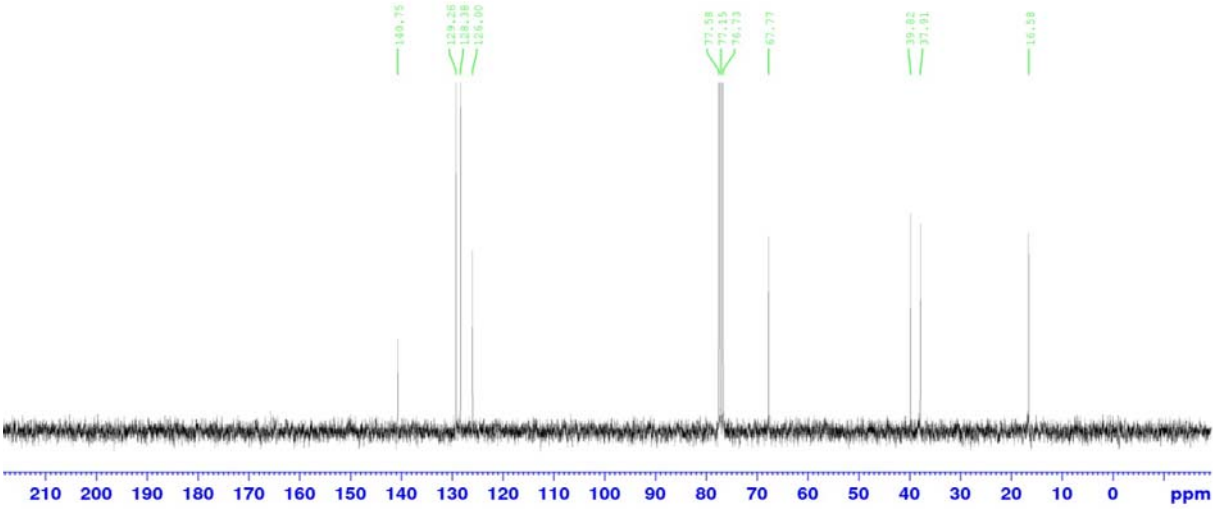




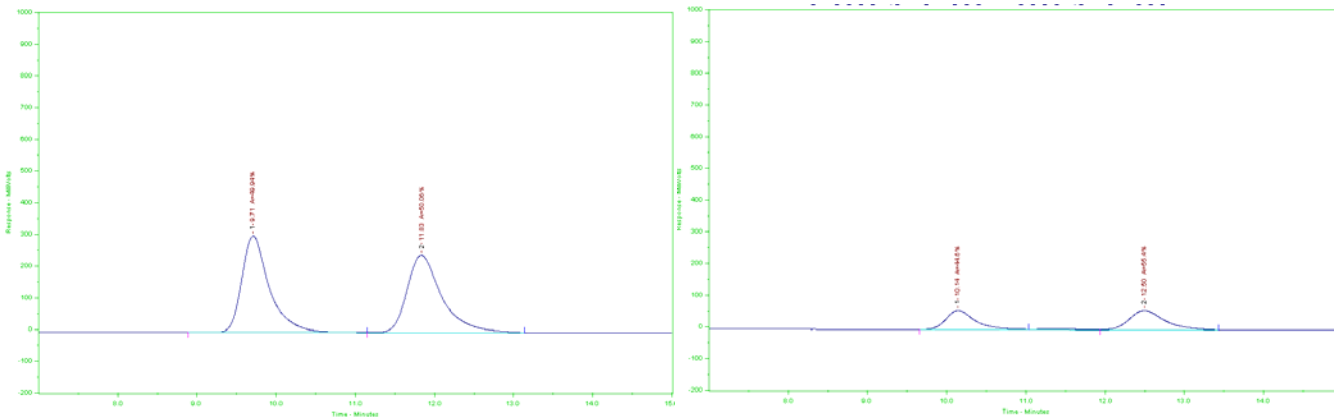
^{13}C NMR



HPLC traces (Chiralpak-OD with OD guard column, 80: 20 hexanes/isopropanol @ 1.0 mL/min)

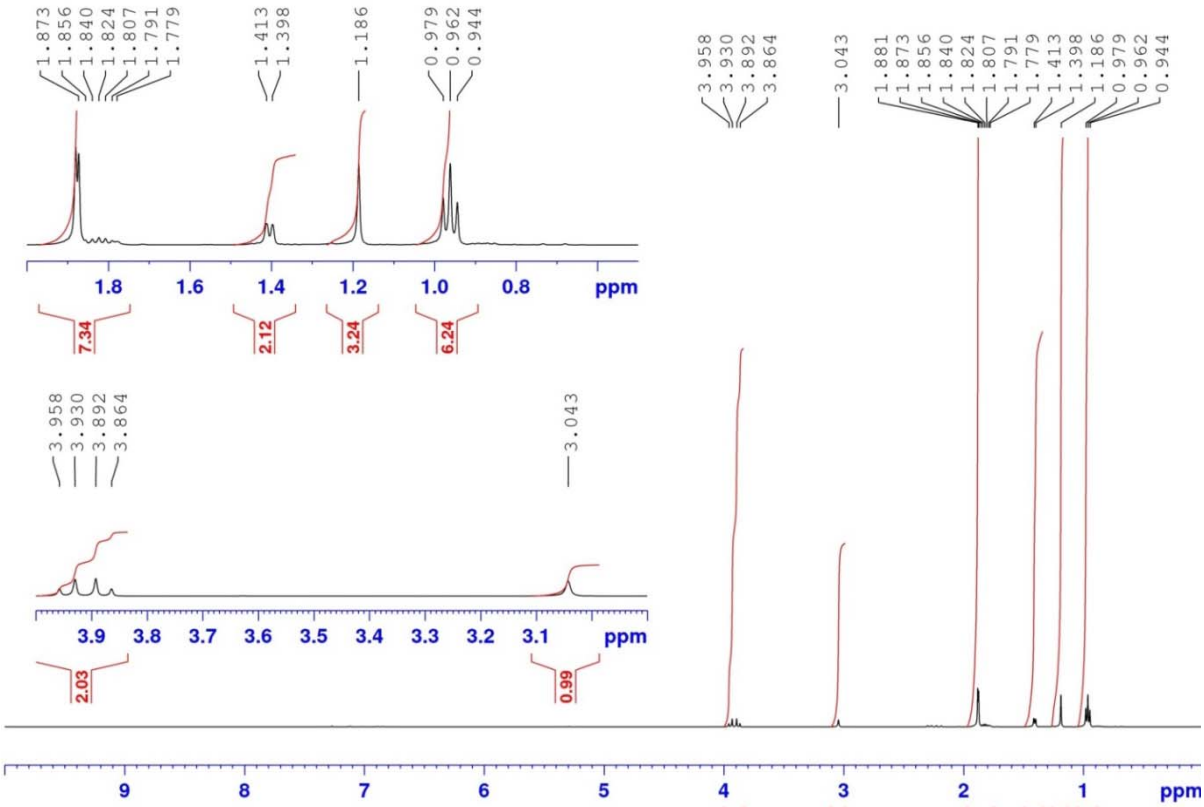
a) racemic mixture

b) after CAHB of **5b** with (*R*,*R*)-**L**

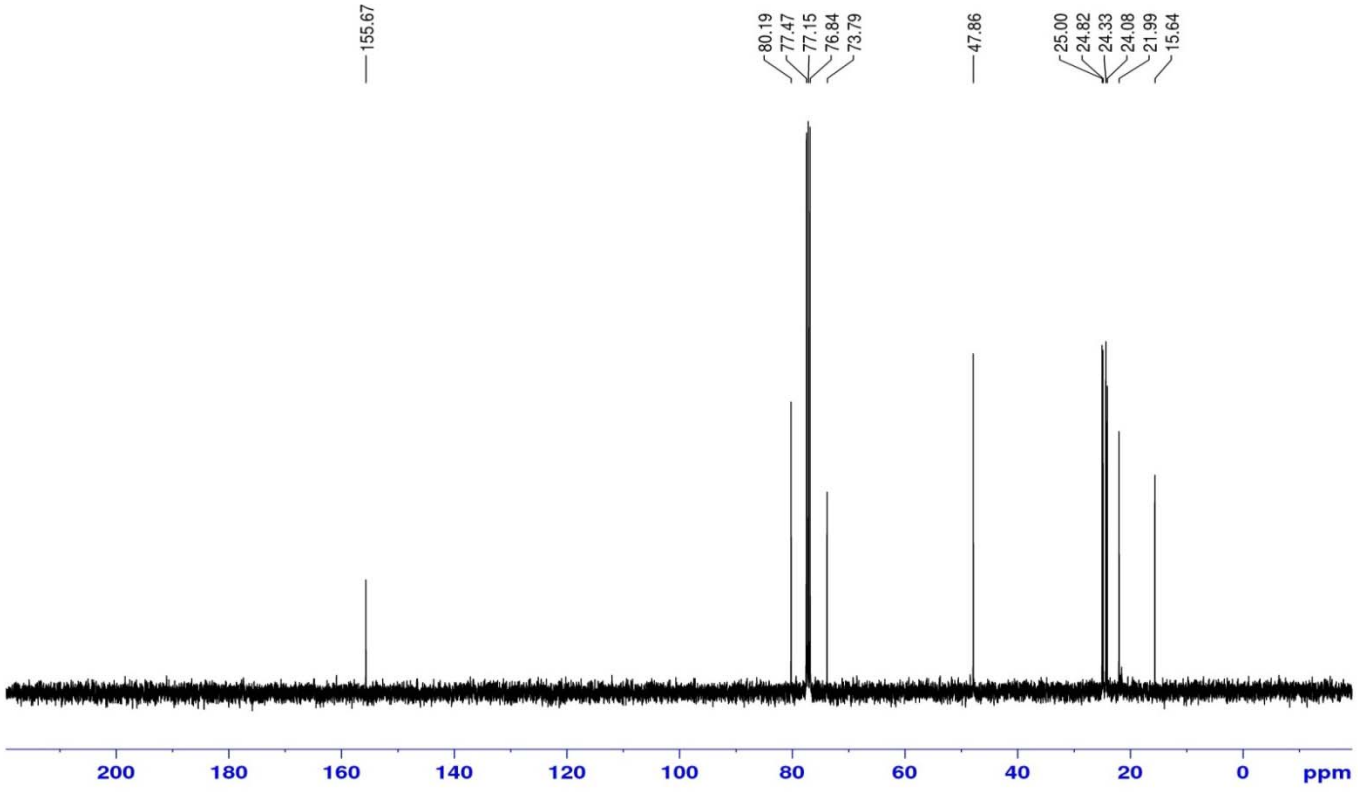


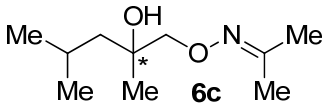
6c

^{1}H NMR



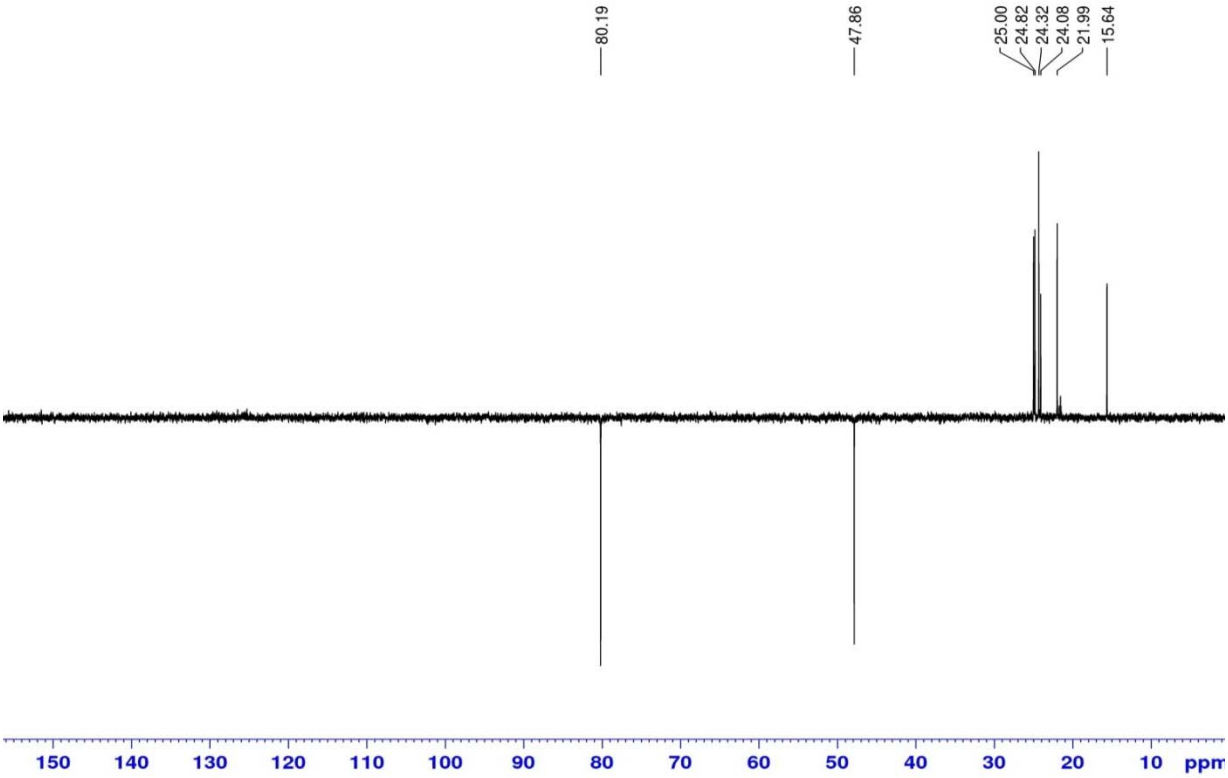
^{13}C NMR



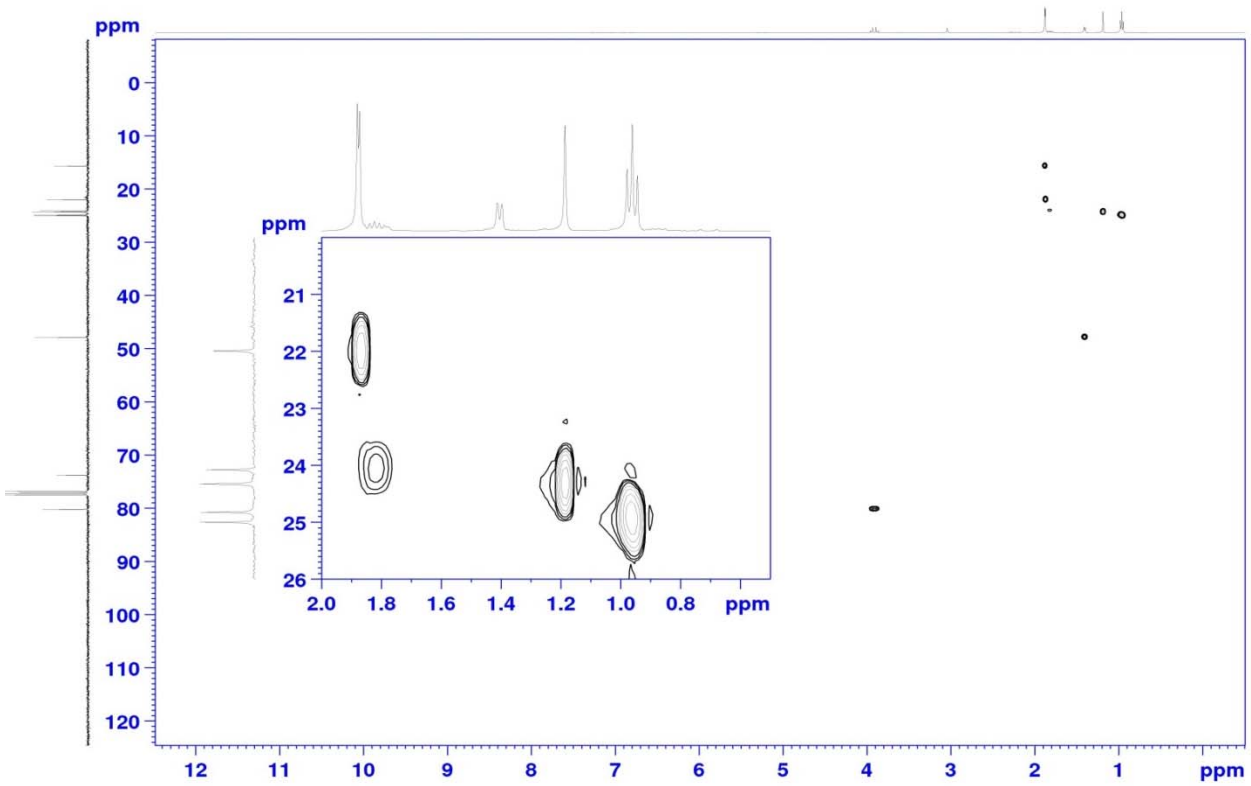


6c

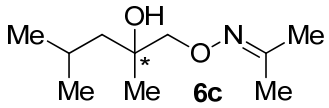
^{13}C DEPT135 NMR

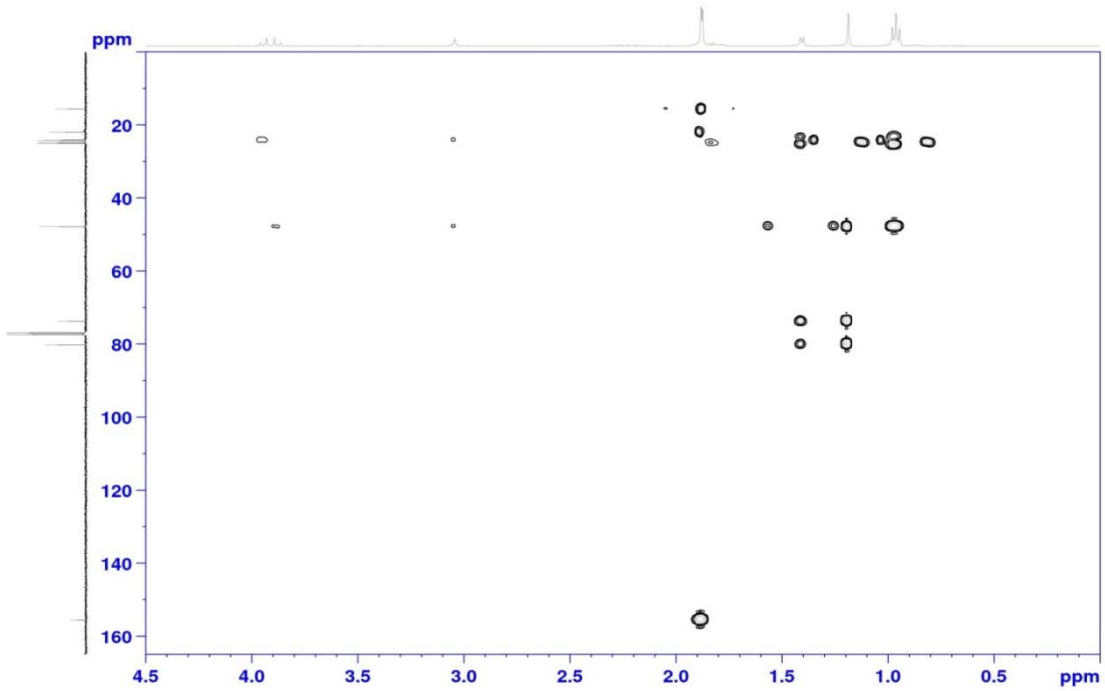


^{1}H-^{13}C HSQC NMR



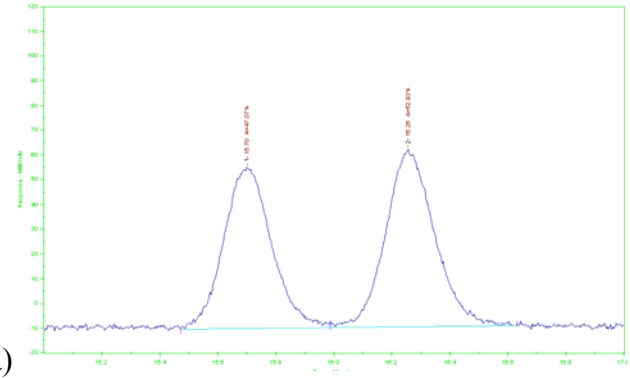
^{1}H-^{13}C HMBC NMR



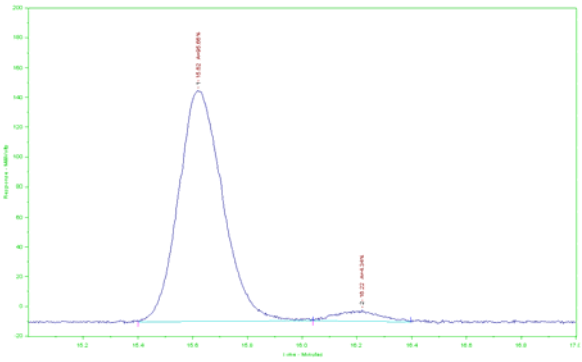


GC traces (Cyclosil β, 90 ˚C isoterm) a) racemic mixture b) *S:R* = 96:4 after CAHB of **5c** with (*S*,*S*)-**L** and c) *S:R* = 5:95 after CAHB of **5c** with (*R*,*R*)-**L**

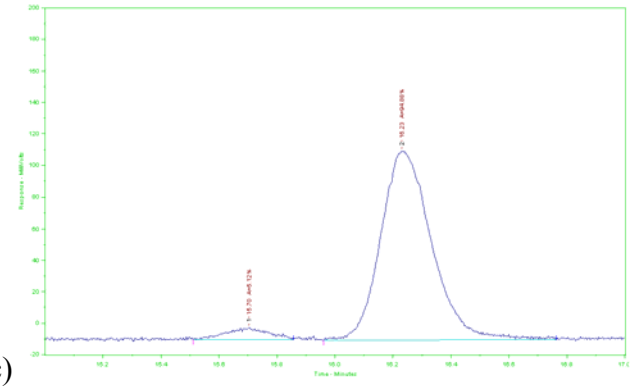
a)

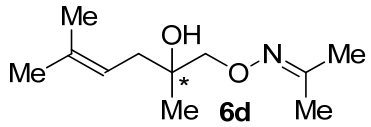


b)

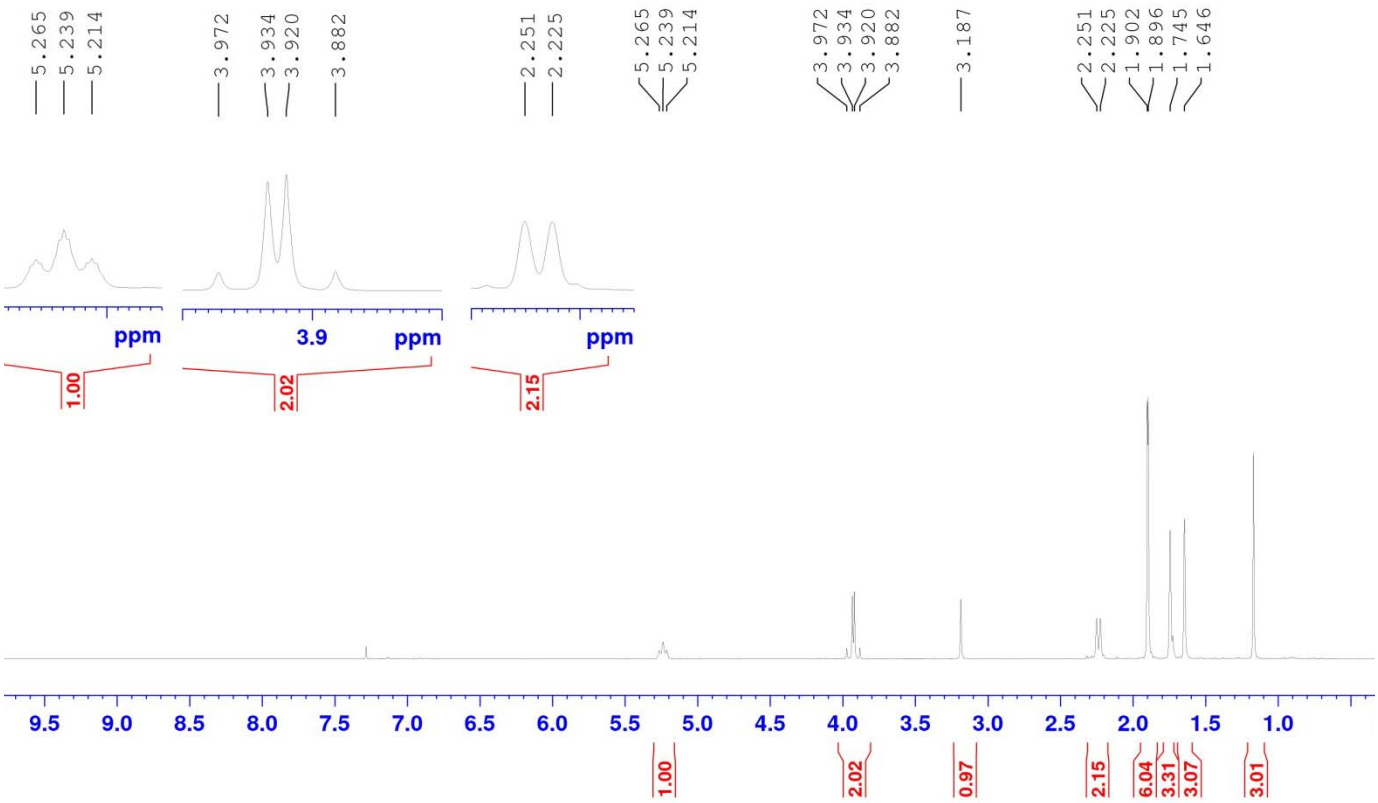


c)

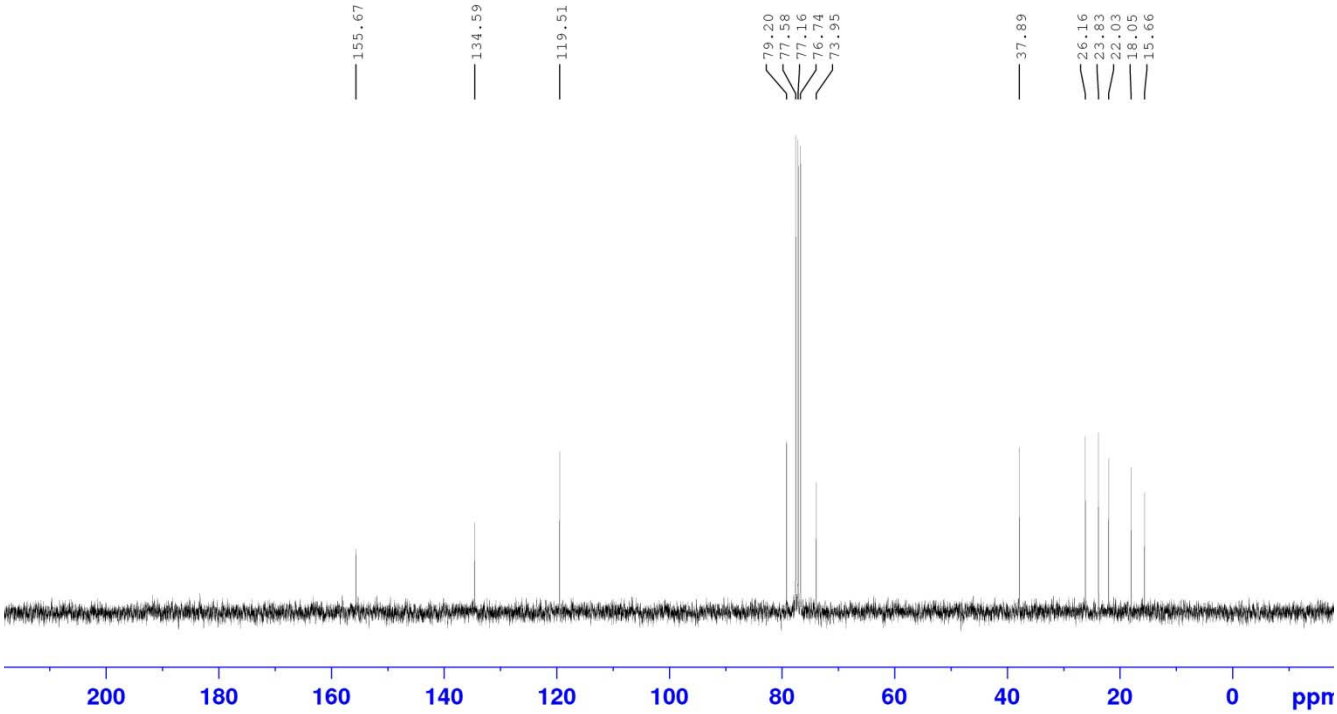


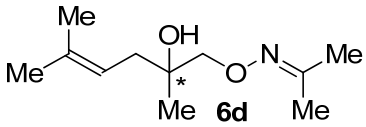


^{1}H NMR

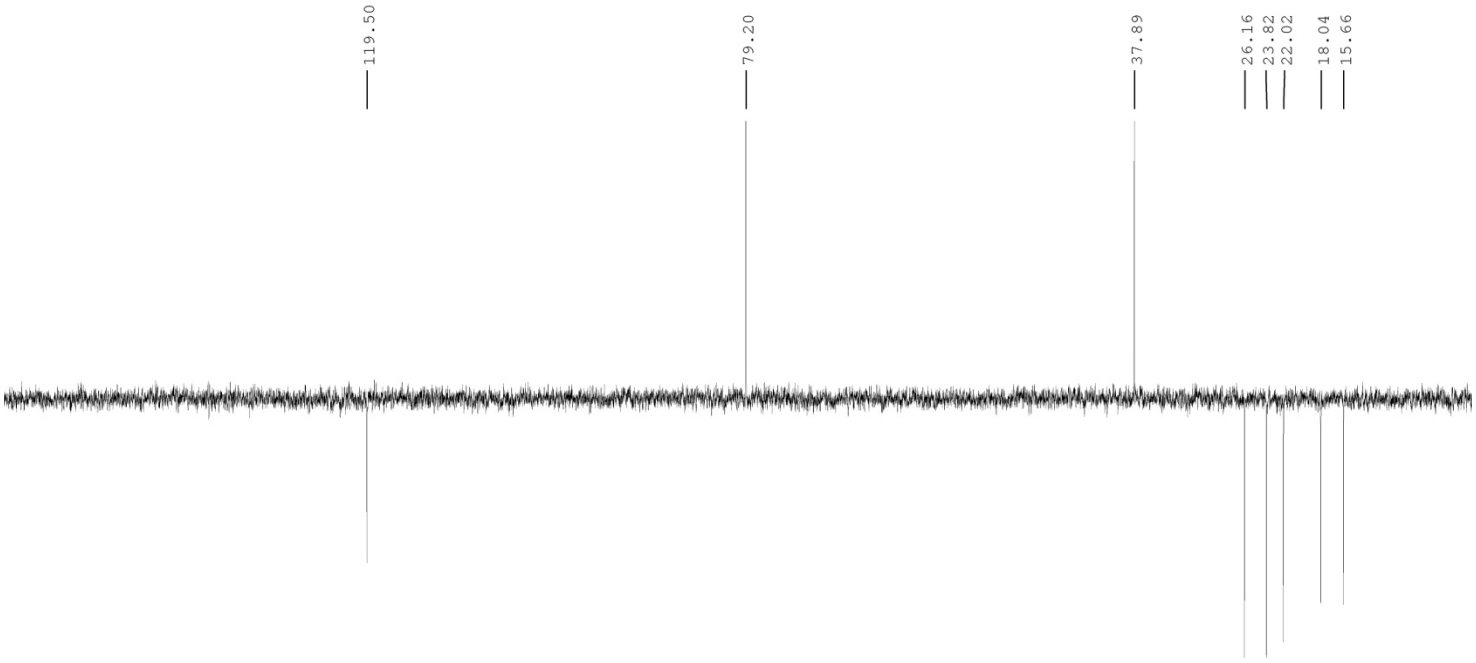


^{13}C NMR

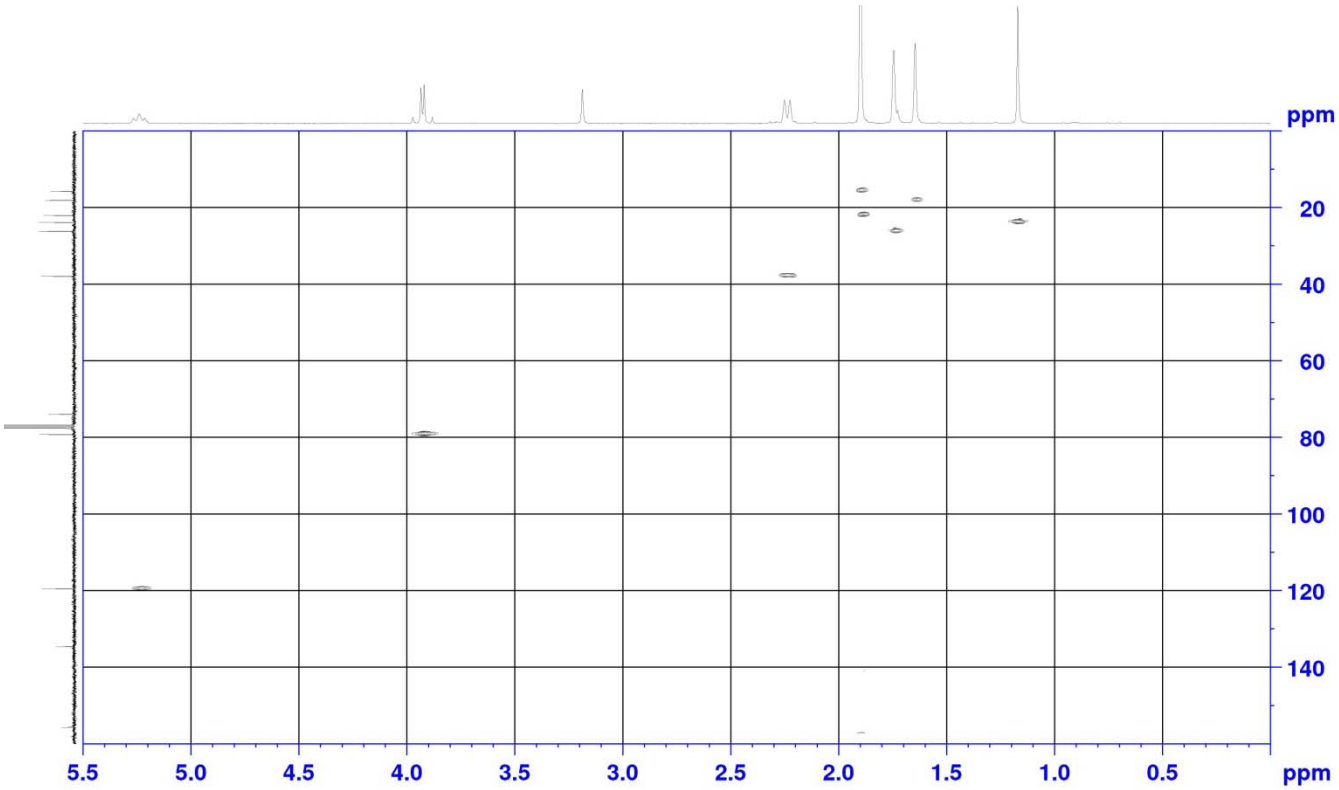




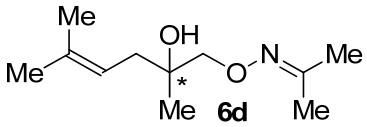
^{13}C DEPT 135 NMR

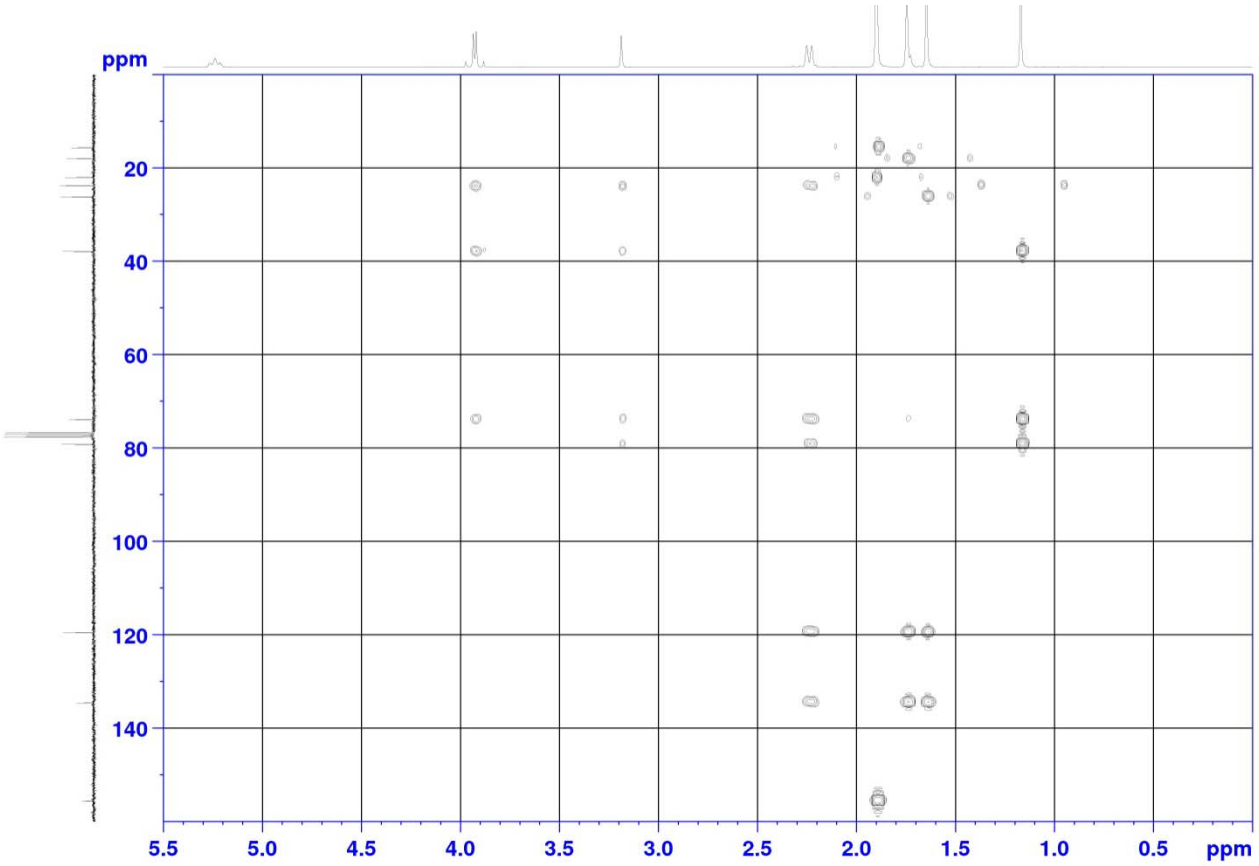


^{1}H- ^{13}C HSQC NMR



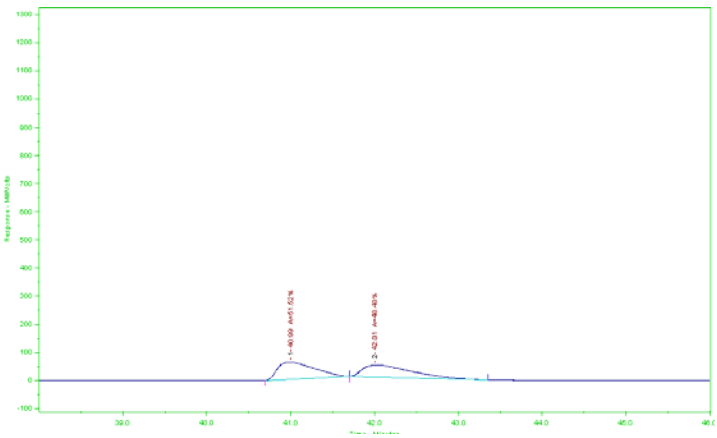
^{1}H- ^{13}C HMBC NMR



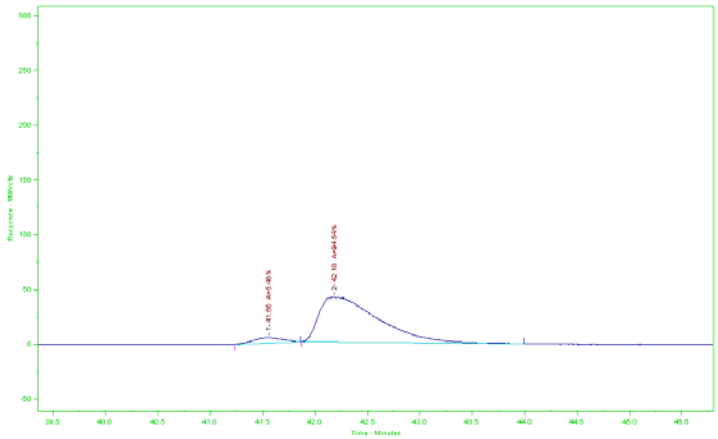


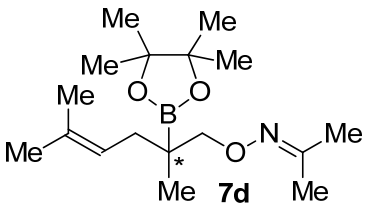
GC traces (CP Chirasil-DEX CB, 95 ˚C isoterm):

a) racemic mixture

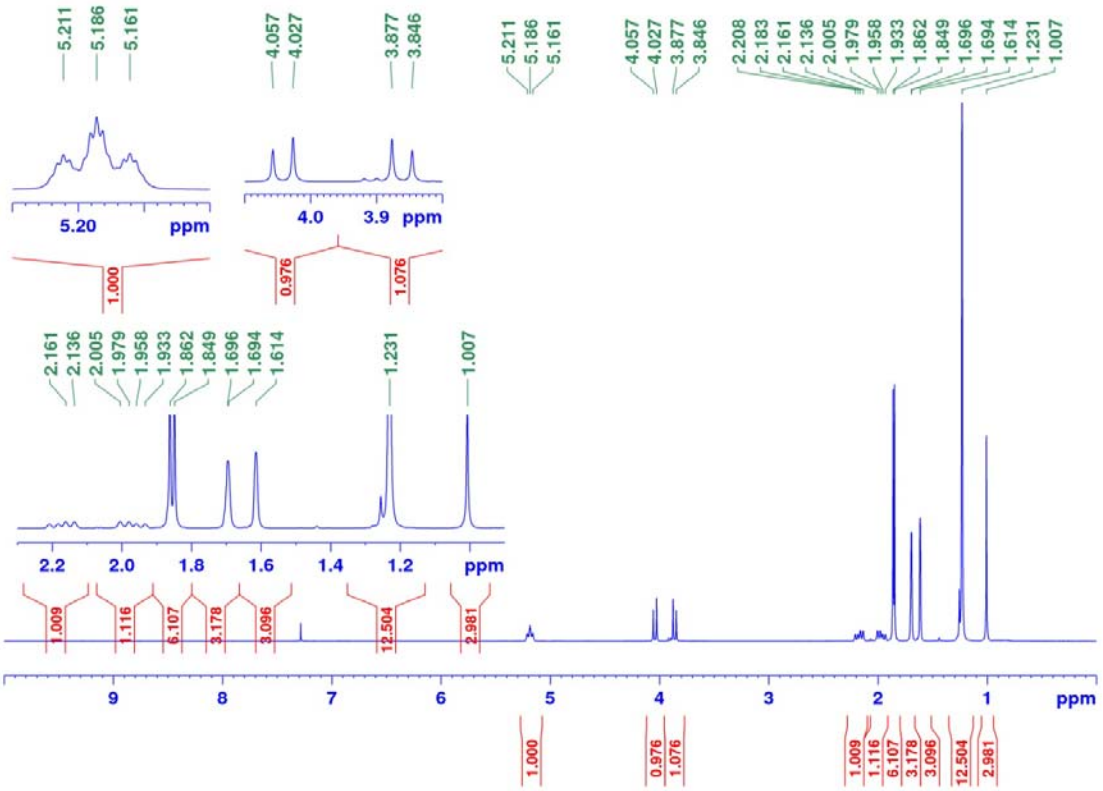


b) *S*:*R* = 5:95 after CAHB of **5d** and (*R*,*R*)-**L**

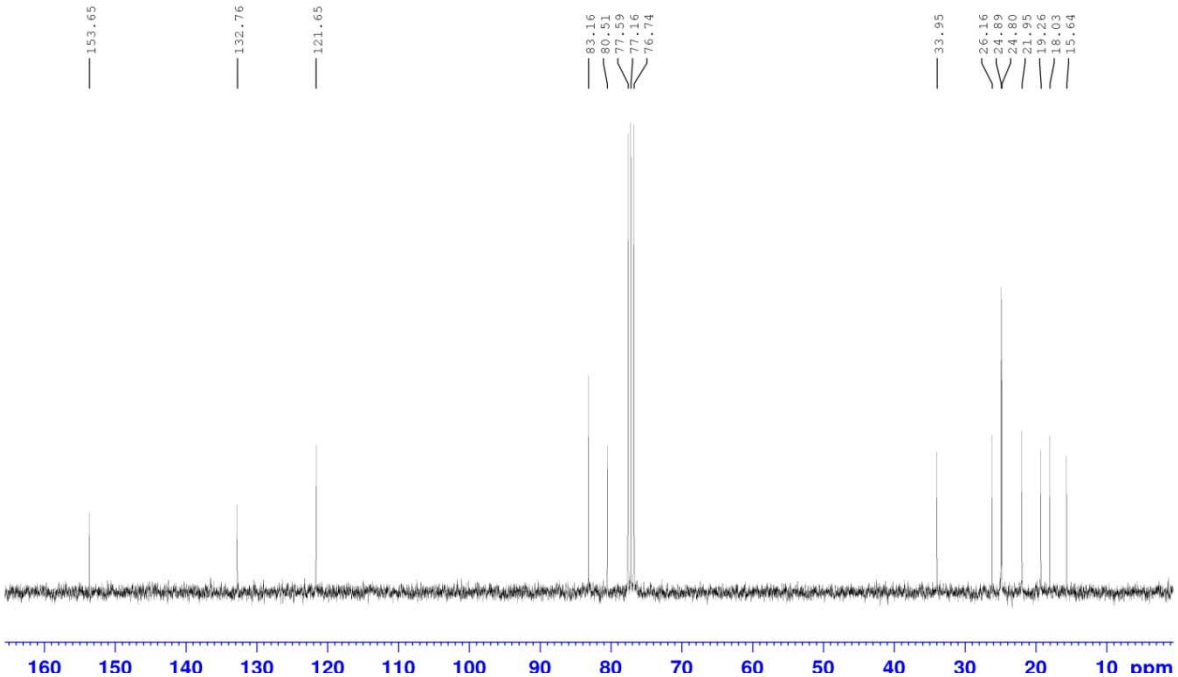


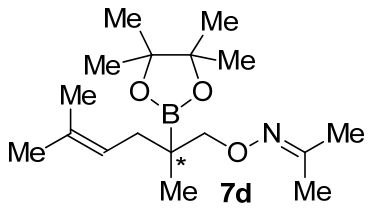


^{1}H NMR



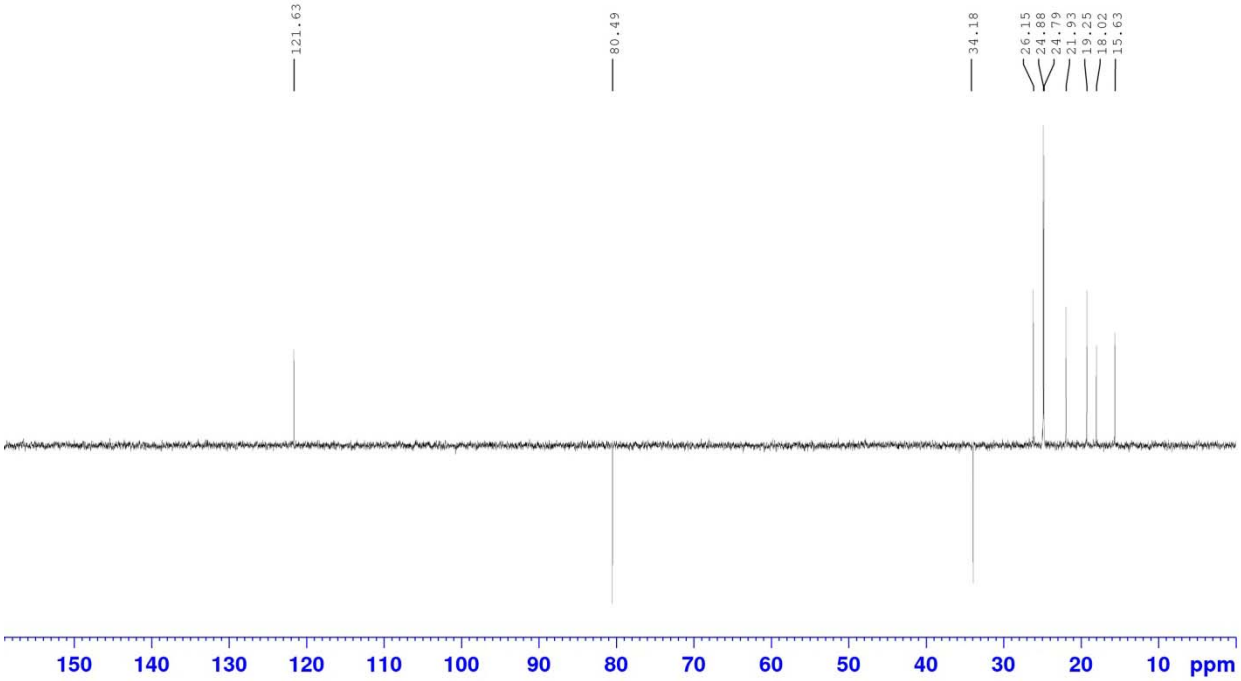
^{13}C NMR



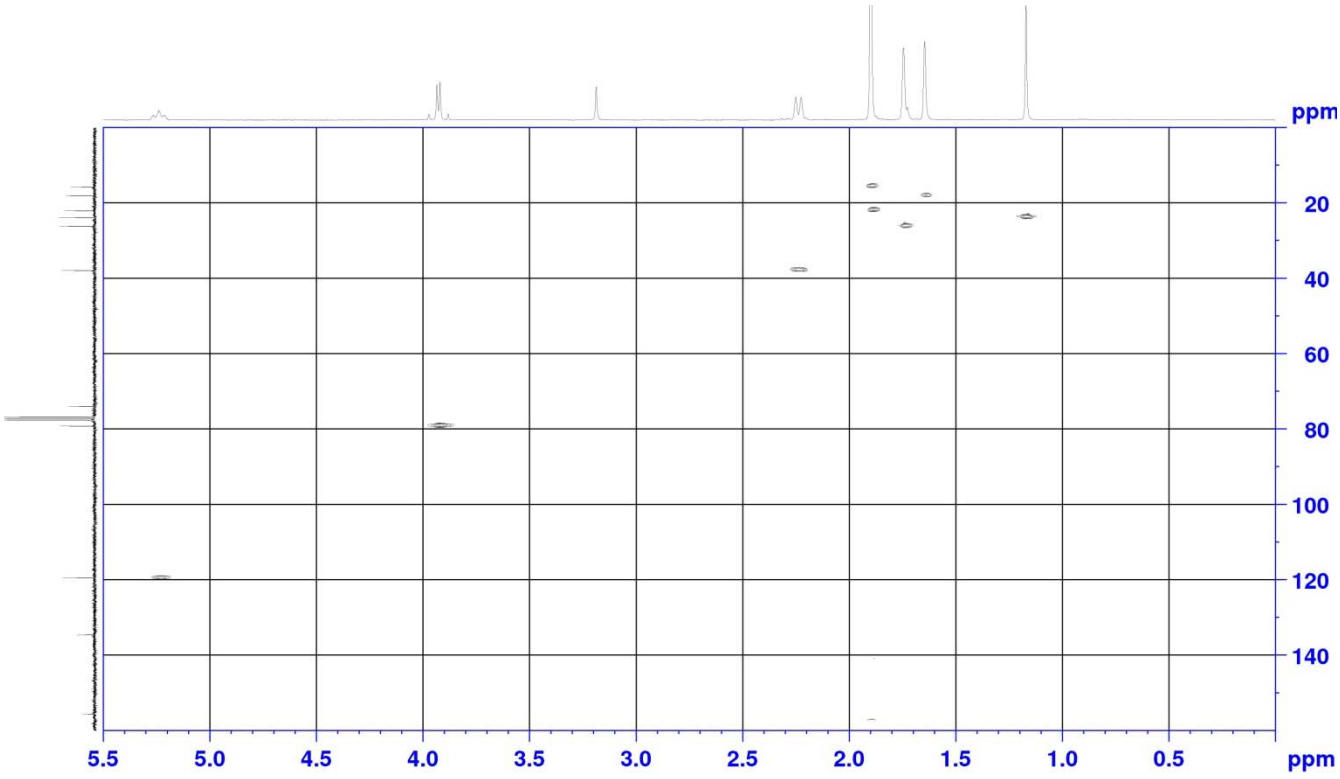


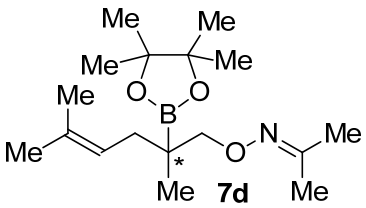
7d

^{13}C DEPT 135 NMR

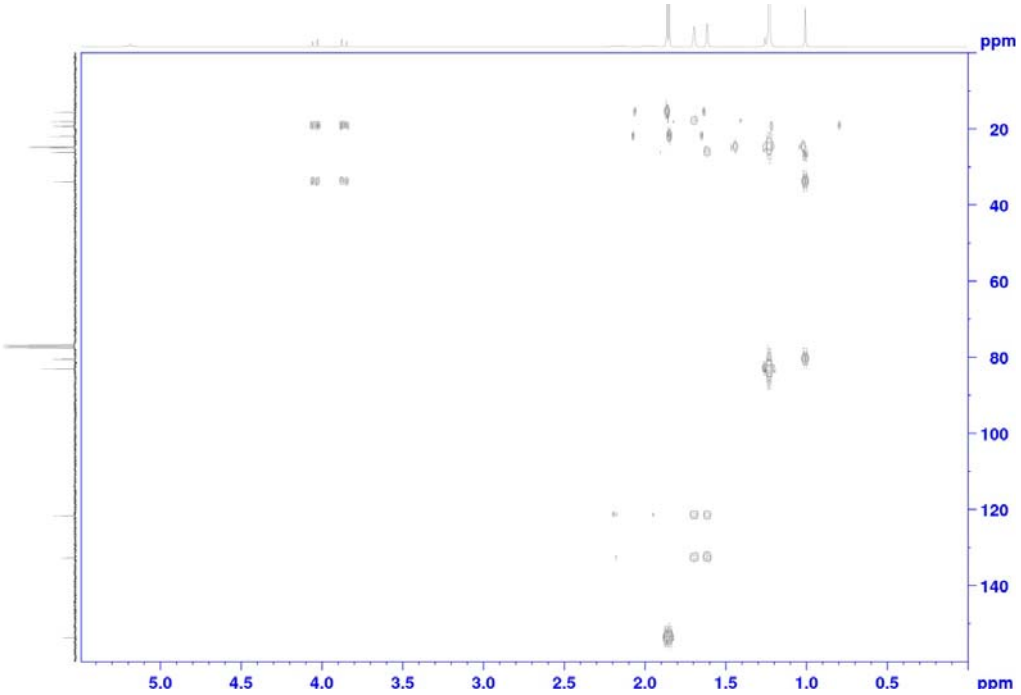


^{1}H- ^{13}C HSQC NMR

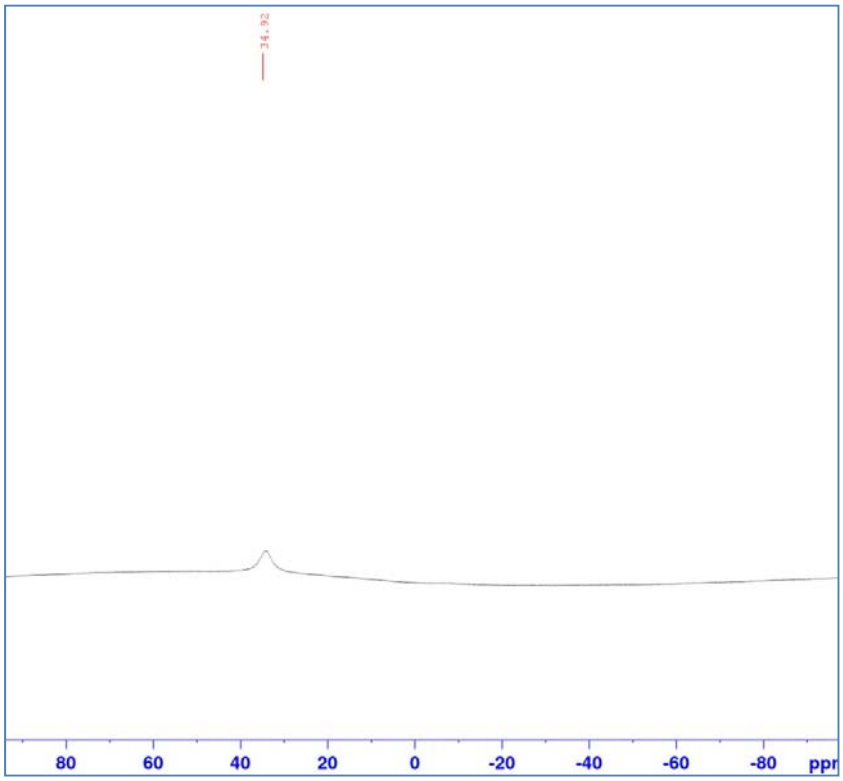




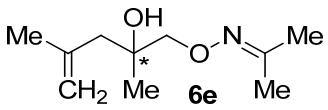
^{1}H- ^{13}C HMBC NMR



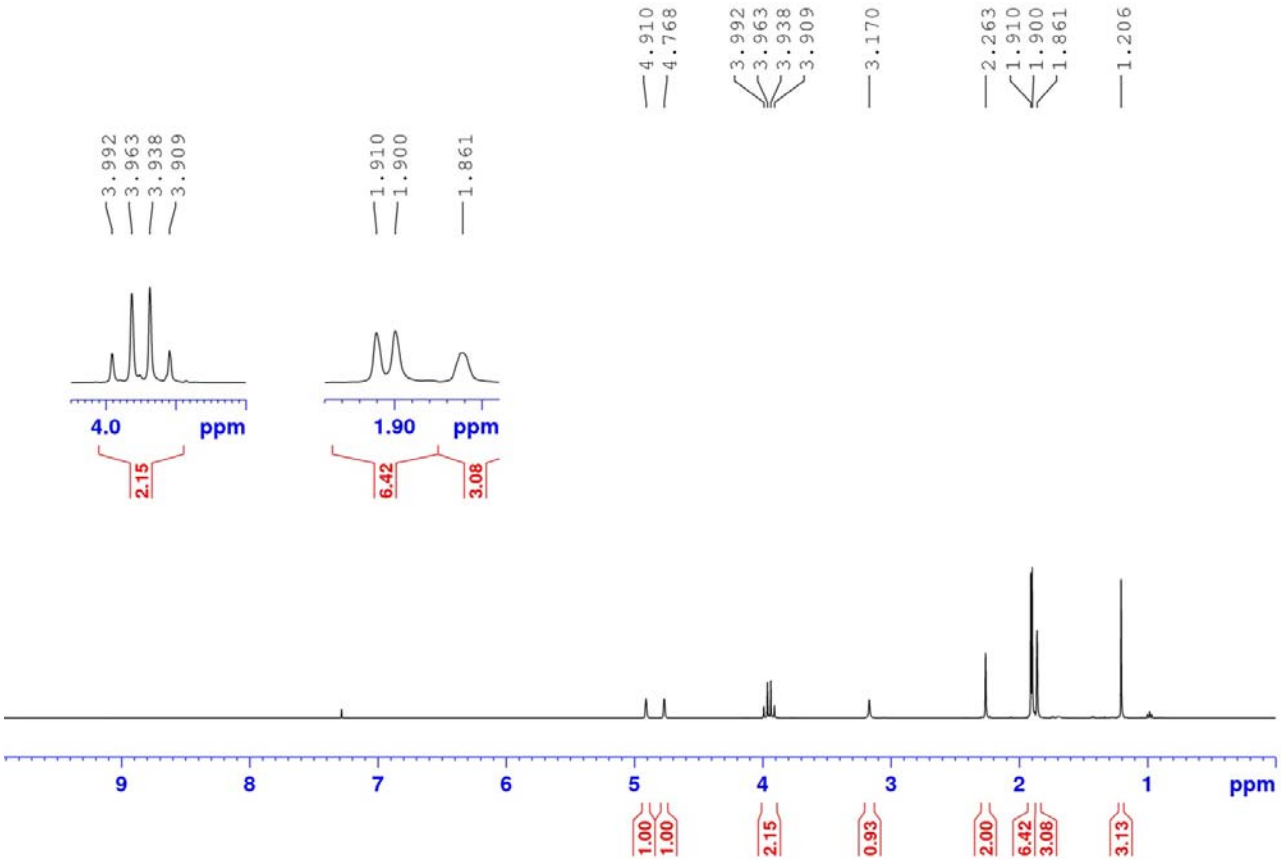
^{11}B NMR



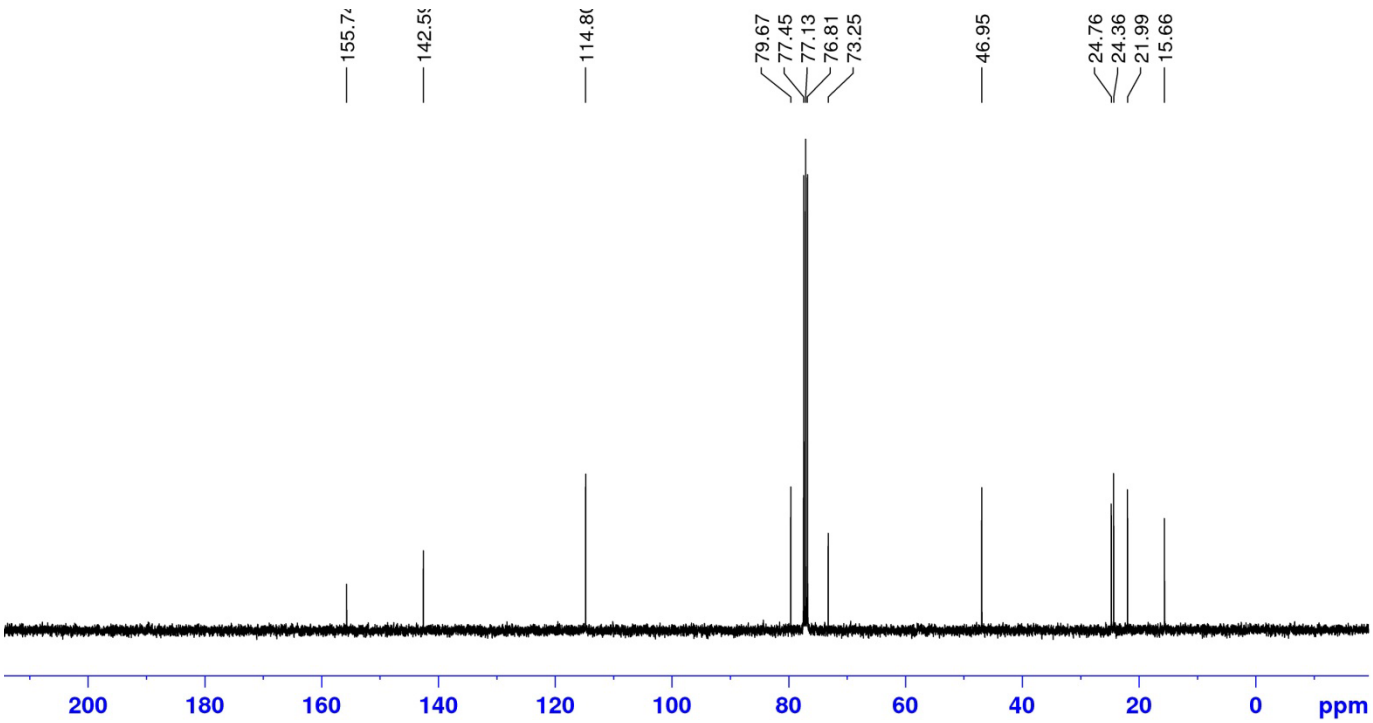
^{1}H NMR

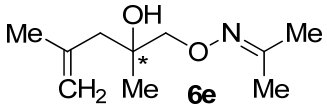


6e



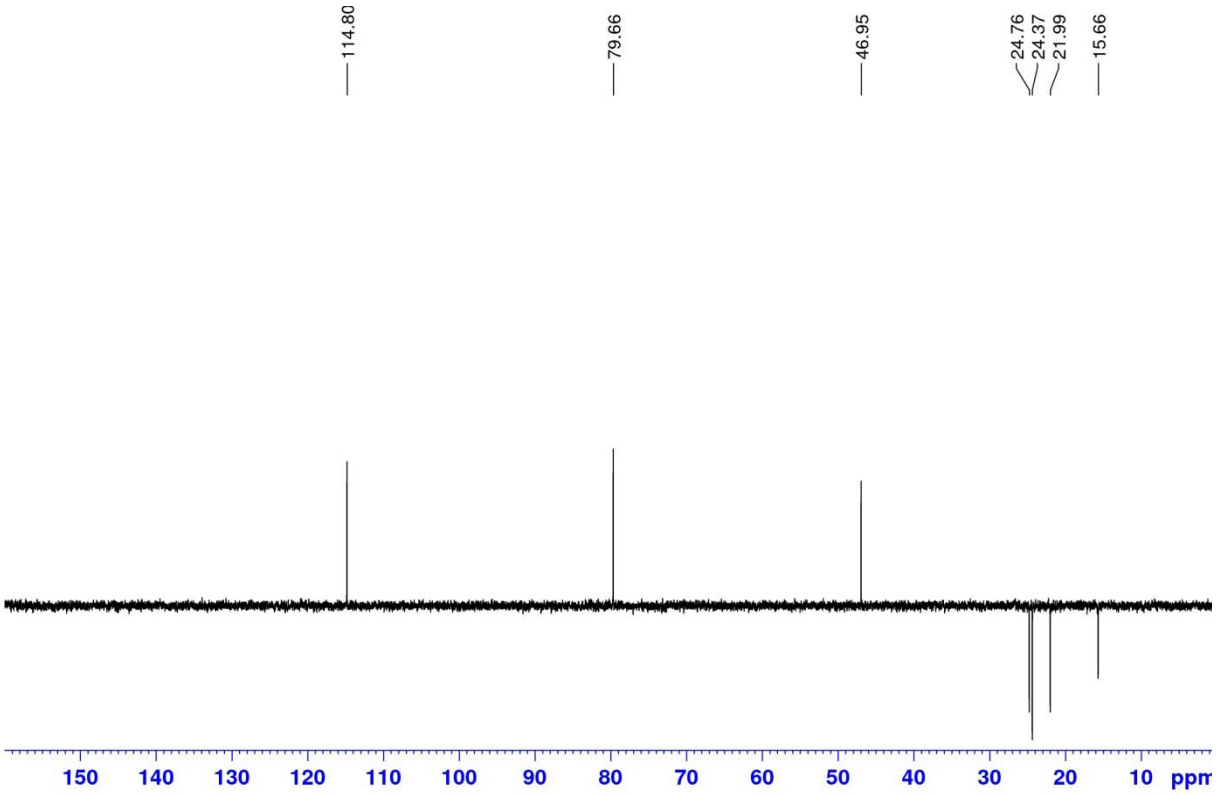
^{13}C NMR



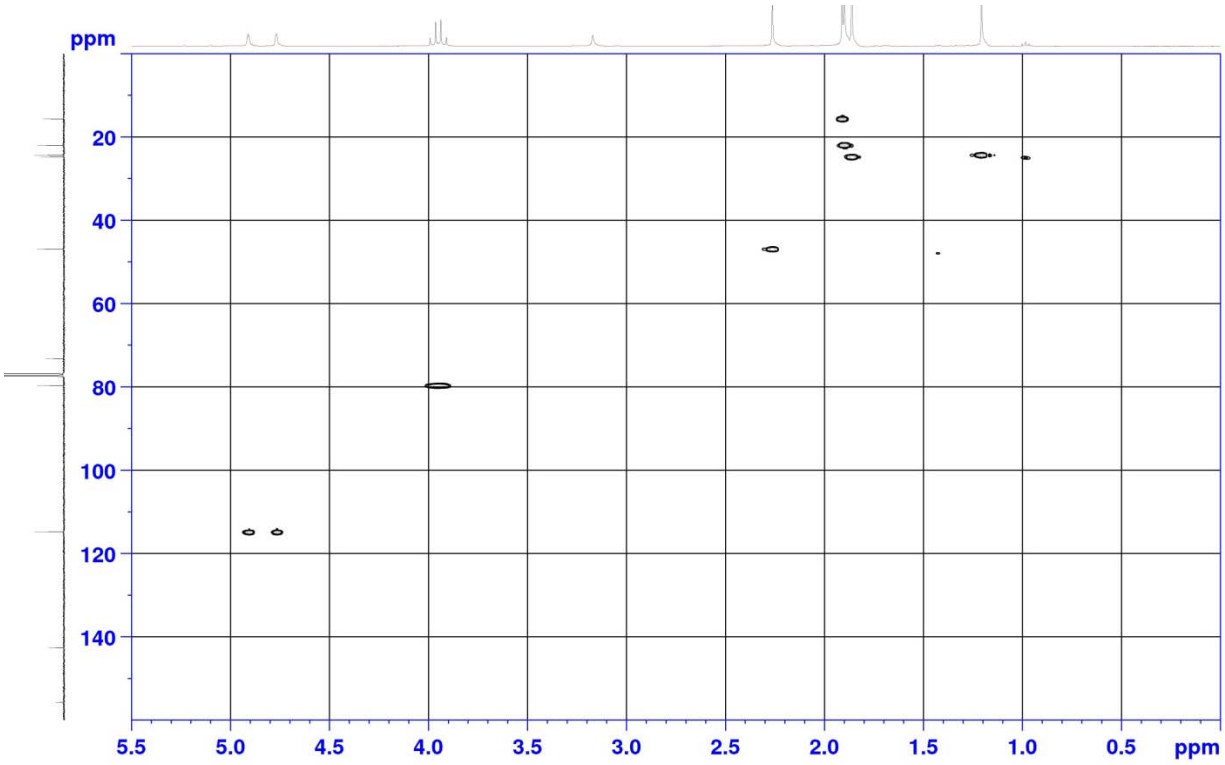


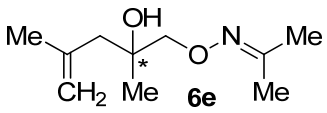
6e

^{13}C DEPT 135 NMR



^{1}H-^{13}C HSQC NMR

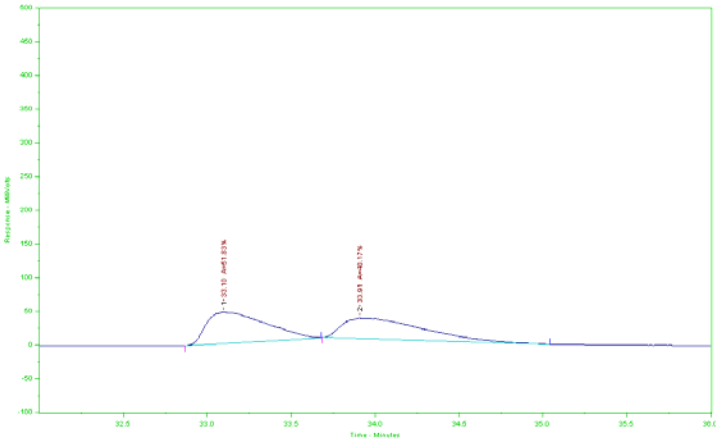




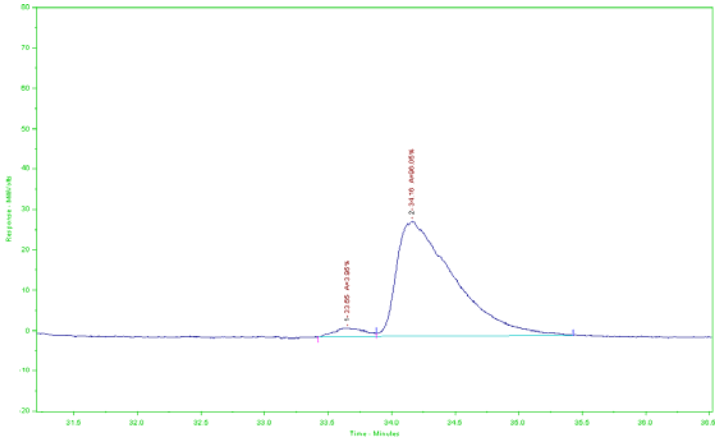
6e

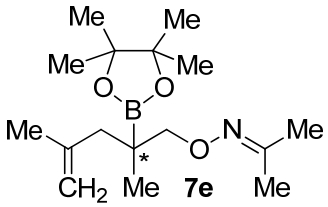
GC traces (CP Chirasil-DEX CB, 85 ˚C isoterm):

a) racemic mixture



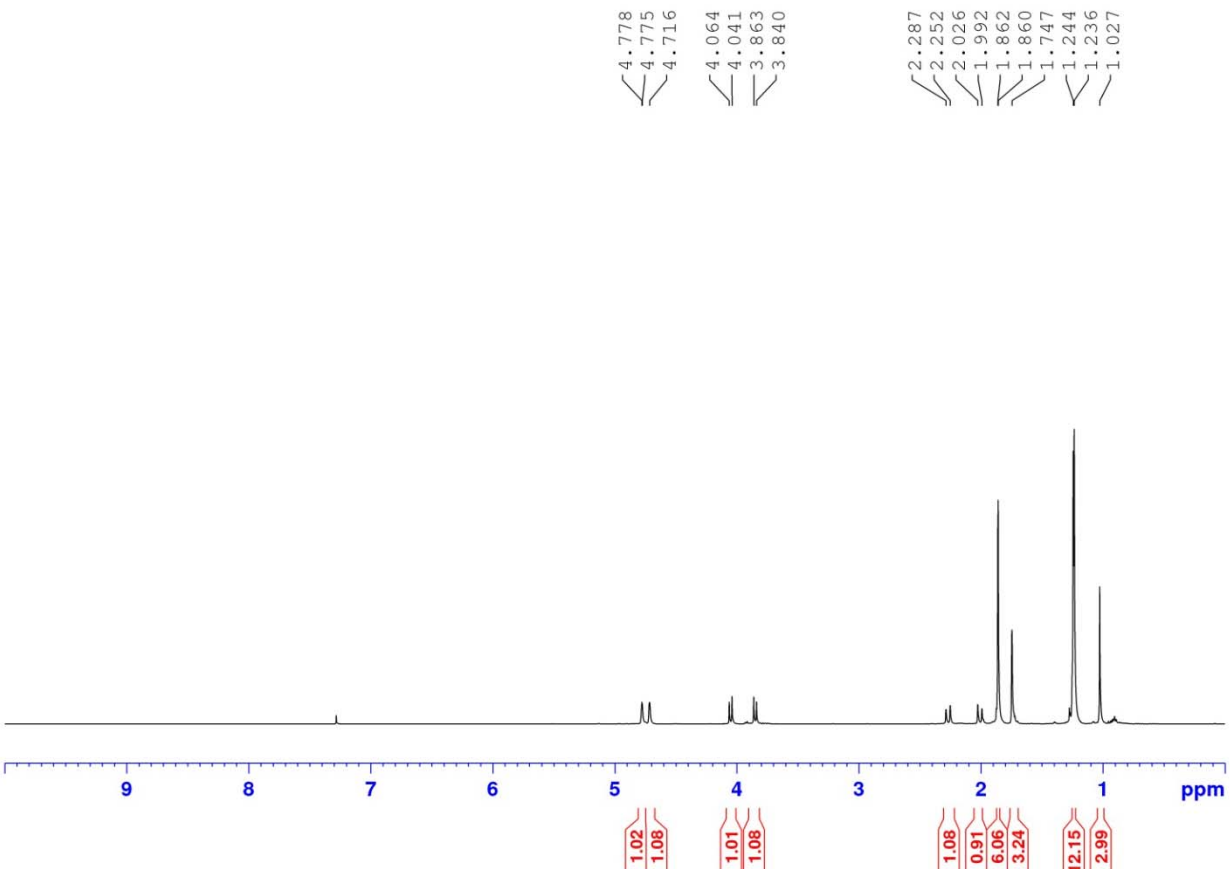
b) *S:R* = 4:96 after CAHB of **5e** with (*R,R*)-L

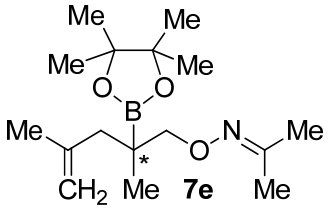




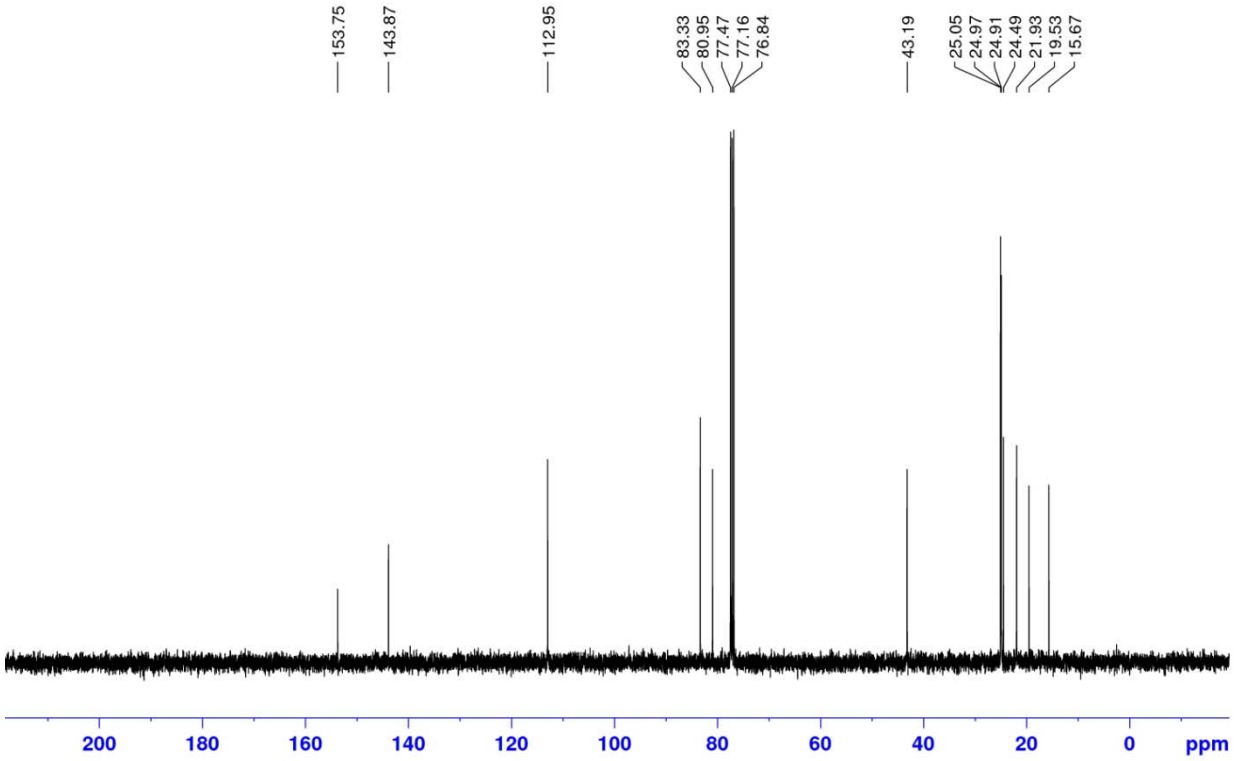
7e

^{1}H NMR

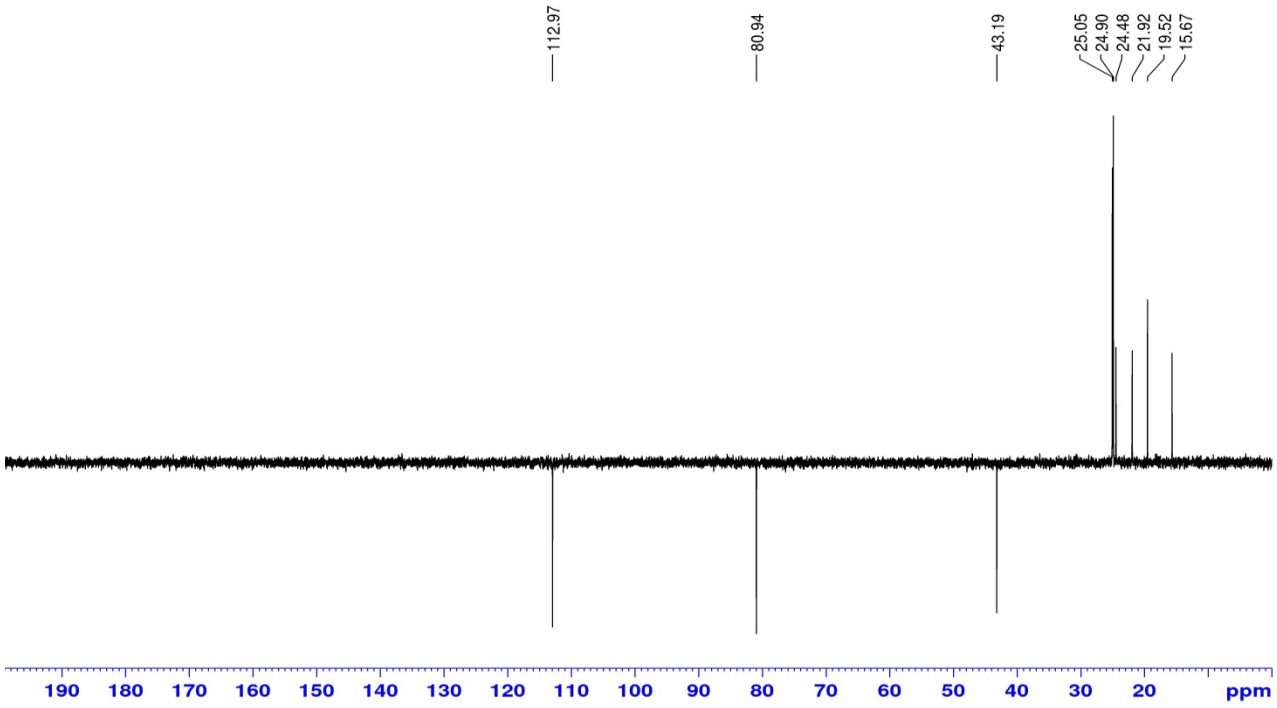


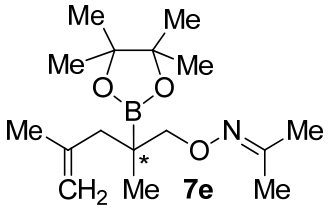


^{13}C NMR

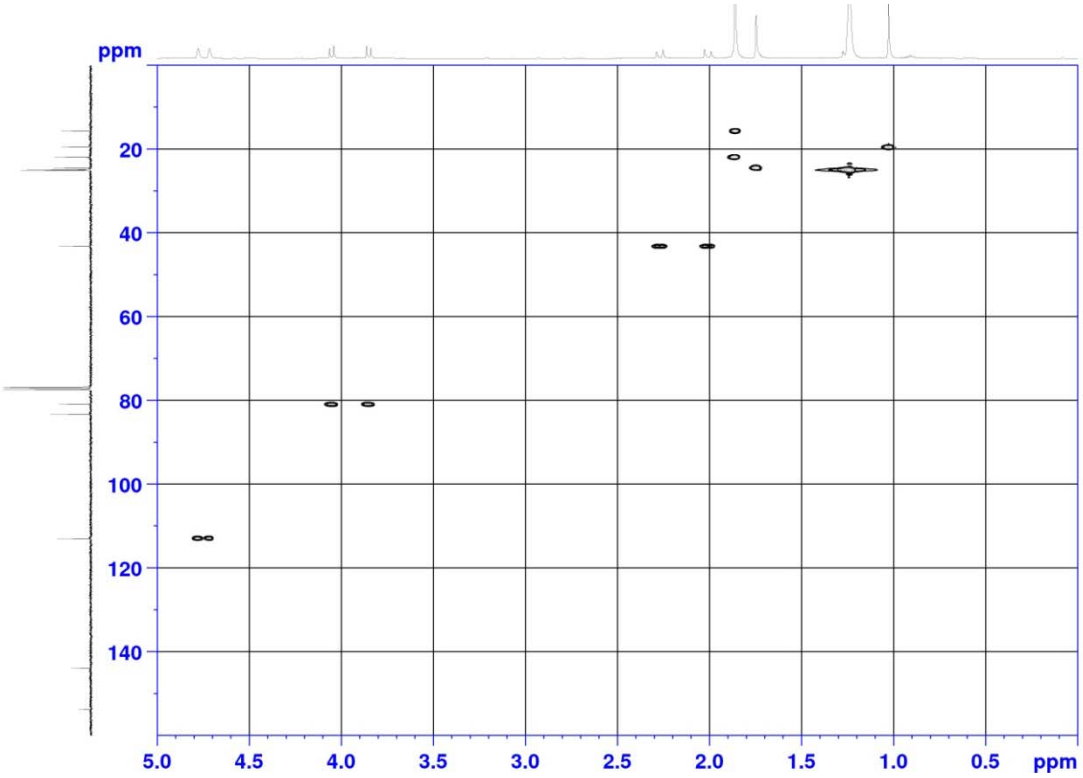


^{13}C DEPT 135 NMR

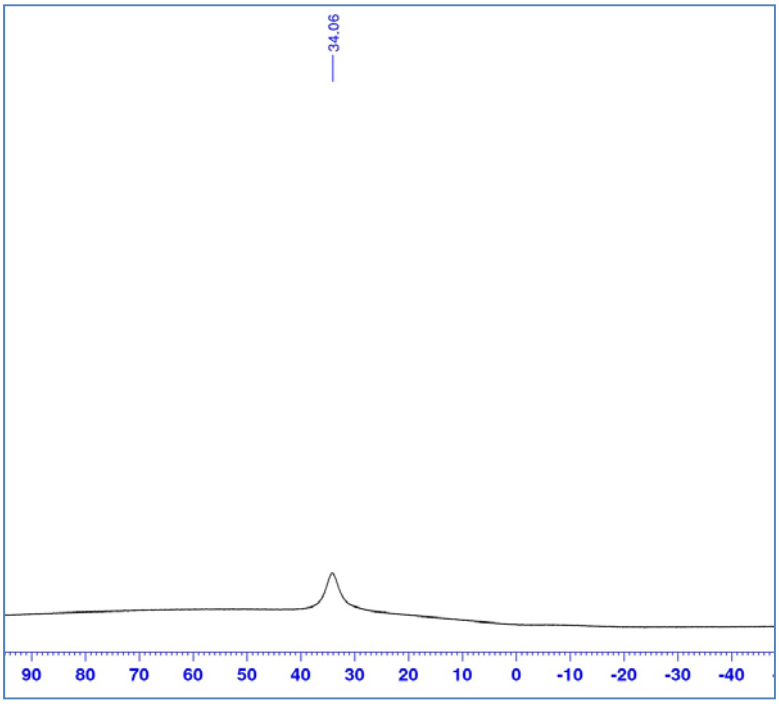


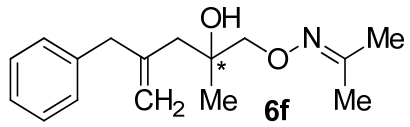


^{1}H-^{13}C HSQC NMR



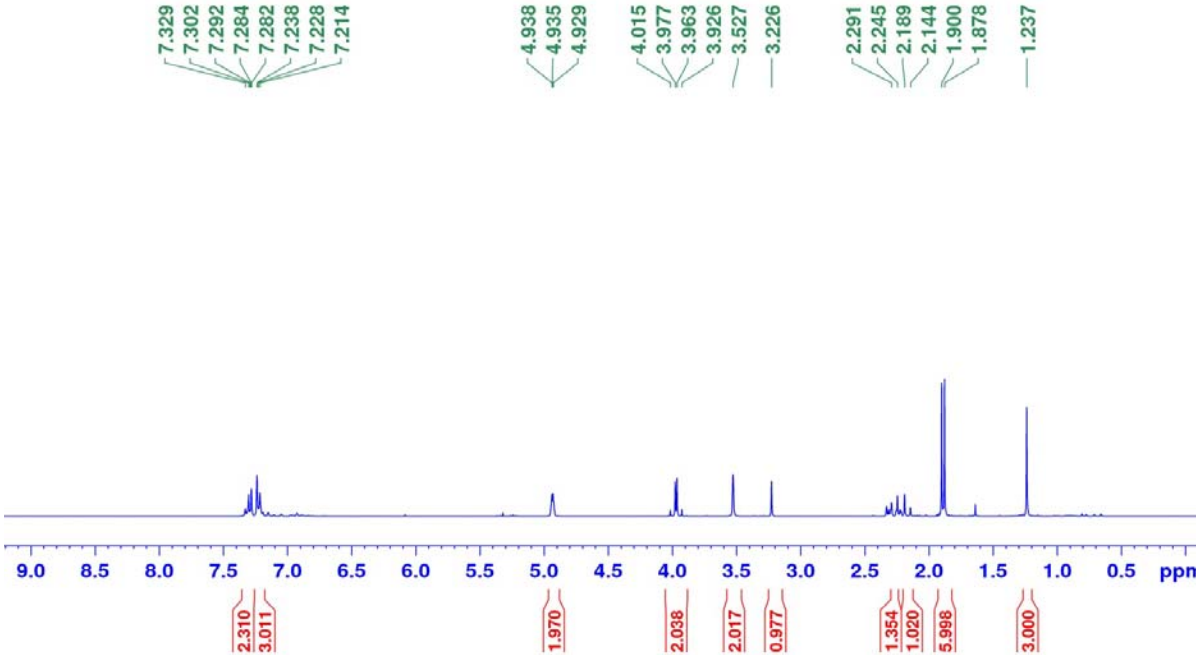
^{11}B NMR



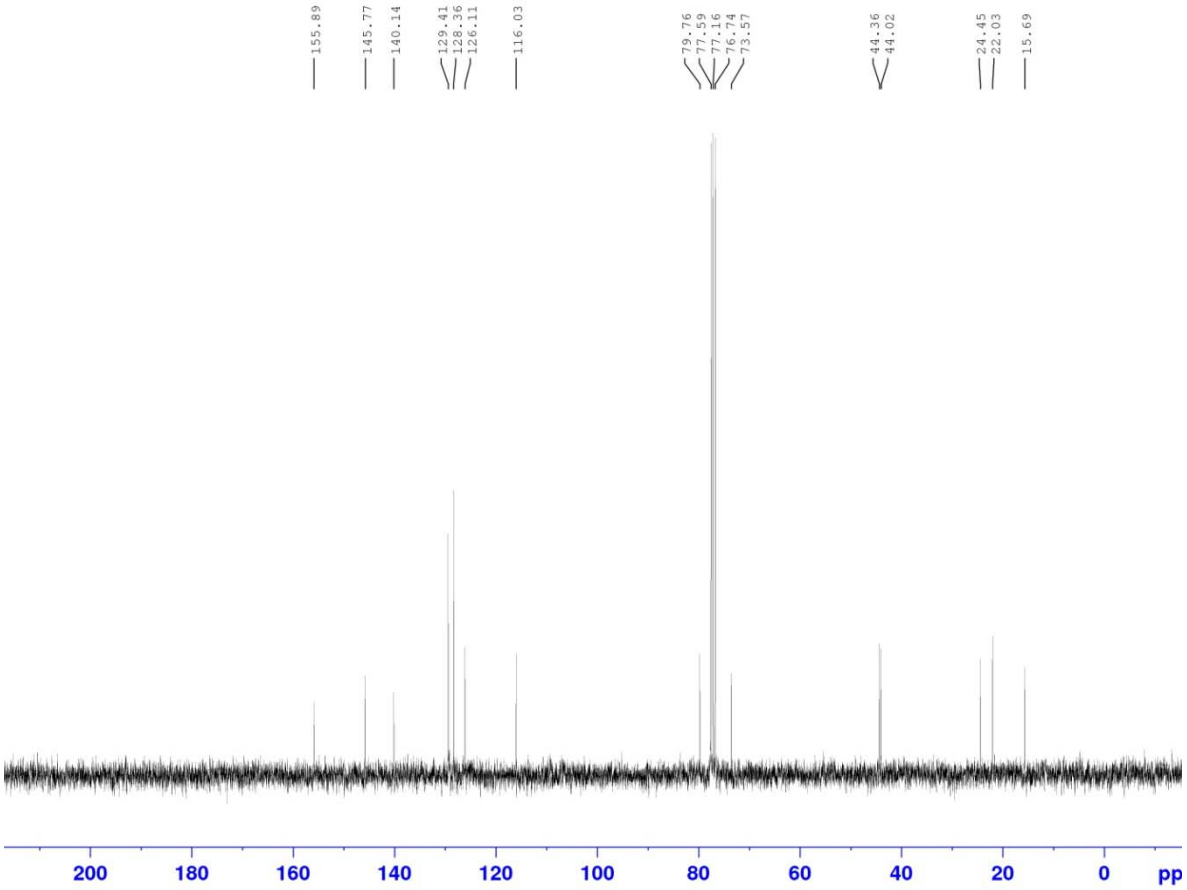


6f

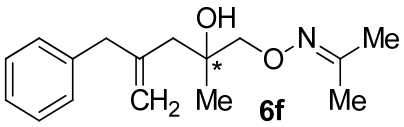
^{1}H NMR

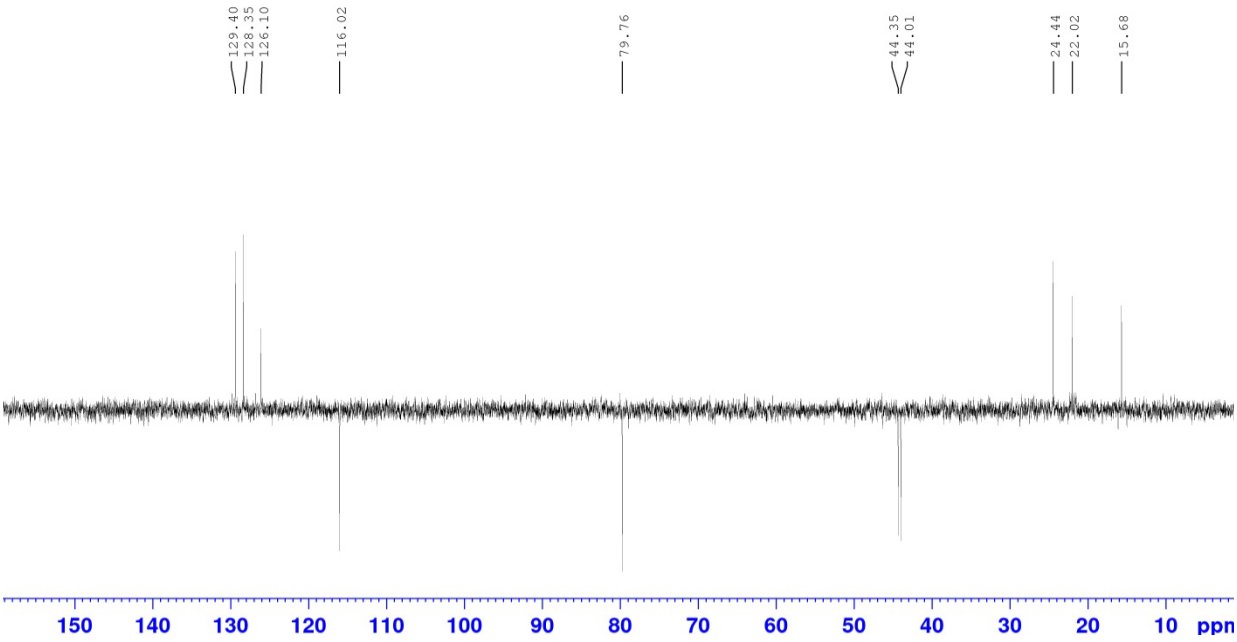


^{13}C NMR

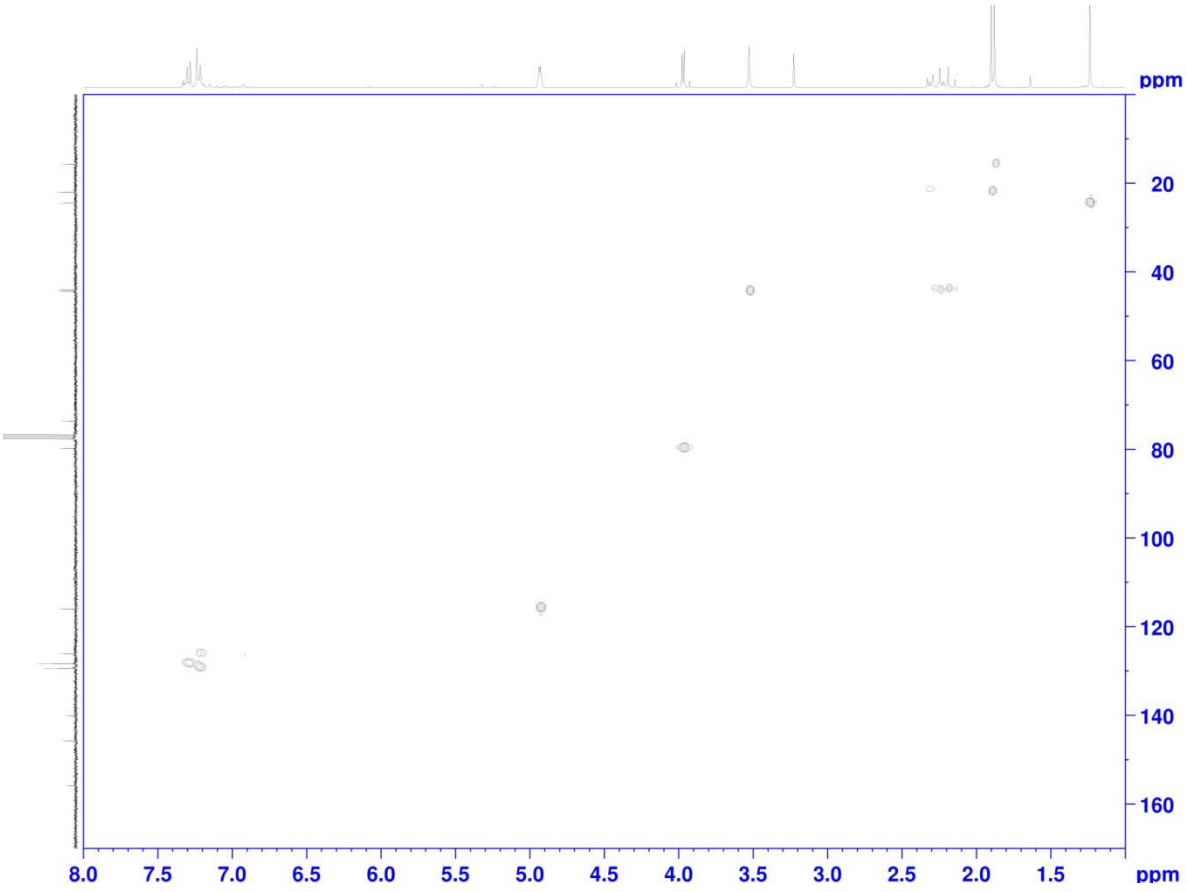


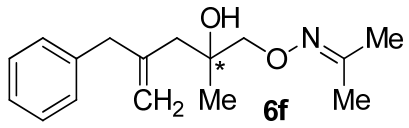
^{13}C DEPT 135 NMR





^{1}H-^{13}C HSQC NMR

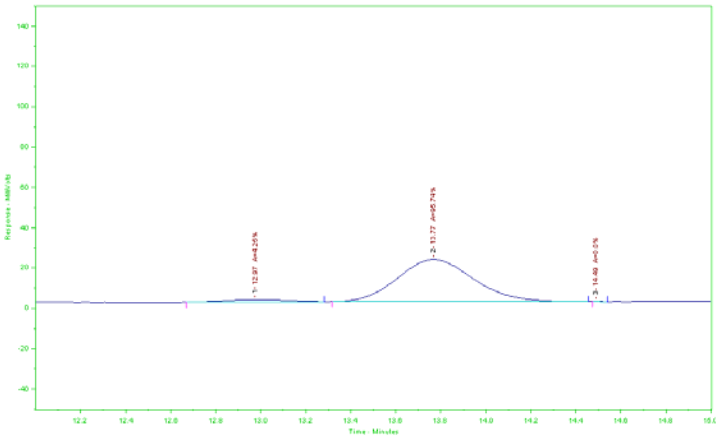




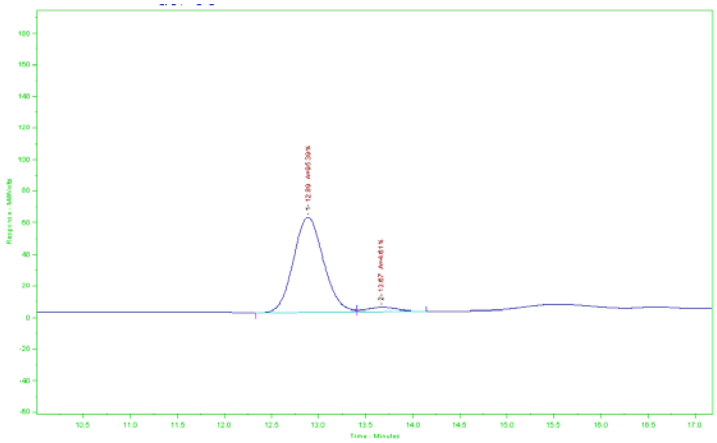
6f

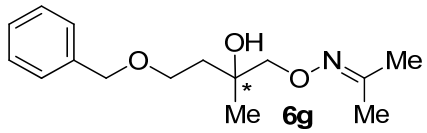
HPLC traces (Chiralpak-AD, 90:10 hexanes/isopropanol @ 1.0 mL/min)

a) *S*:*R* = 4:96 after CAHB of **5f** with (*R*,*R*)-L

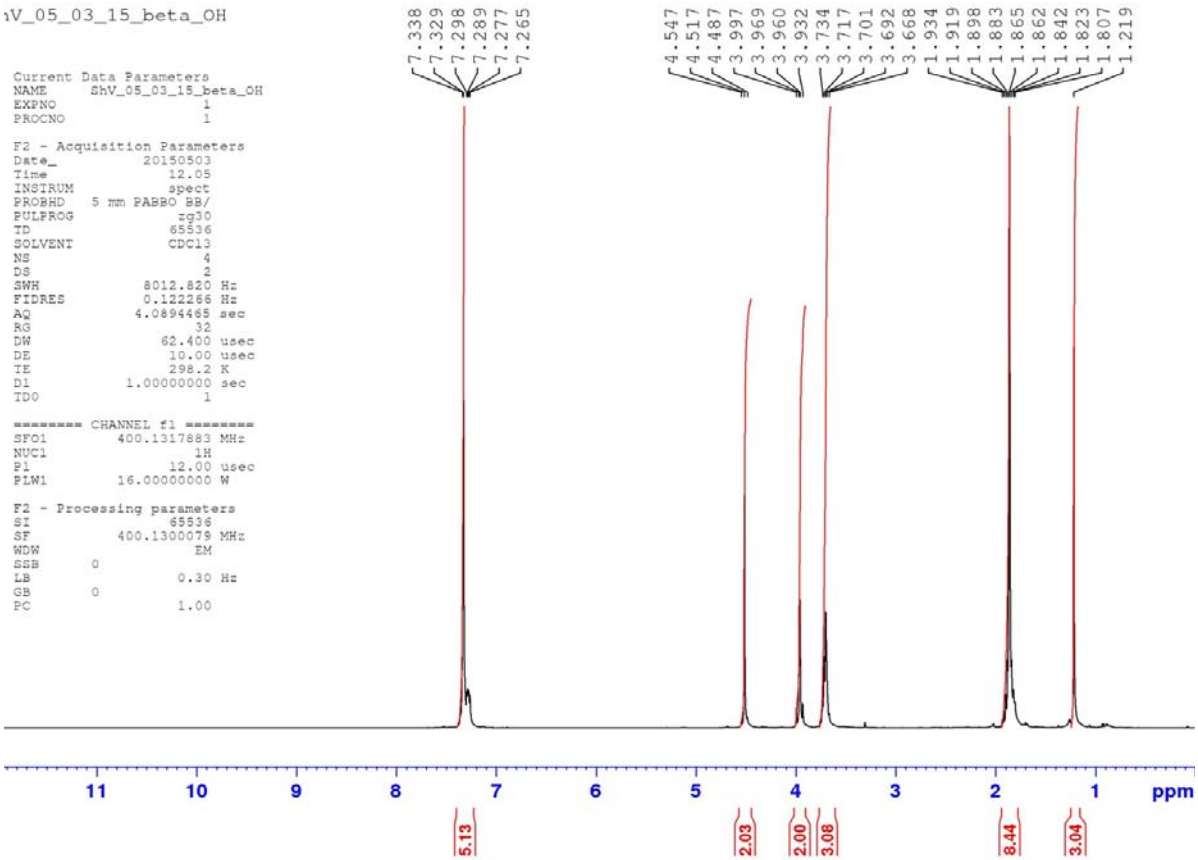


b) *S*:*R* = 95:5 after CAHB of **5f** and (*S*,*S*)-L

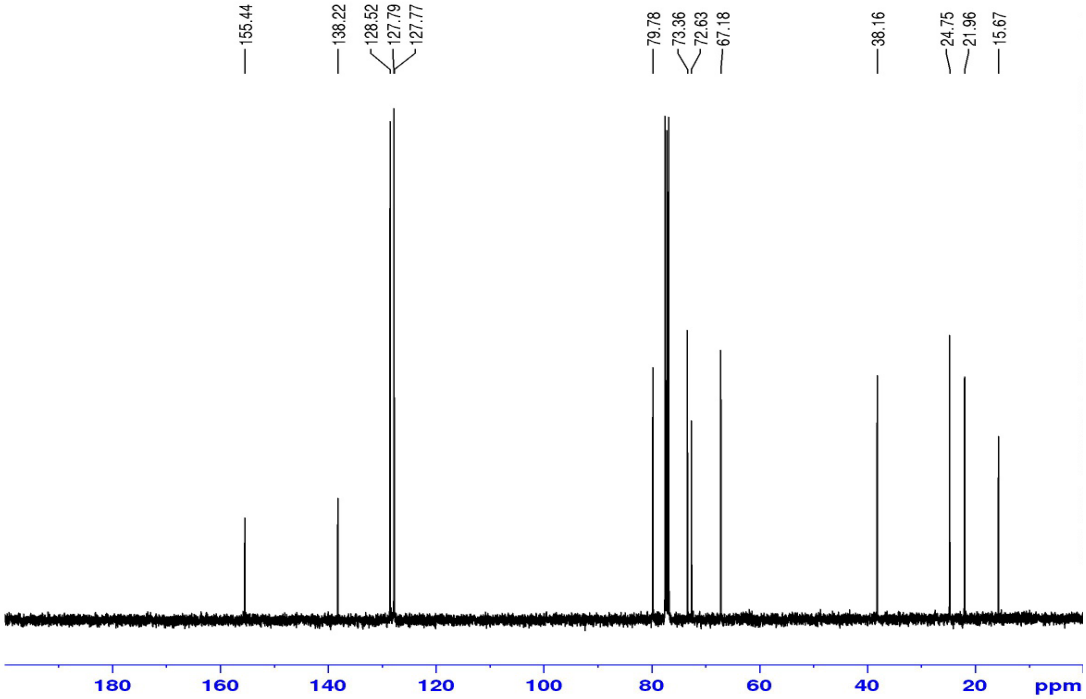


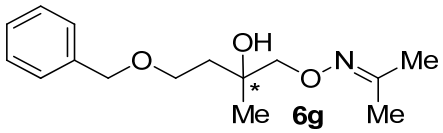


^{1}H NMR

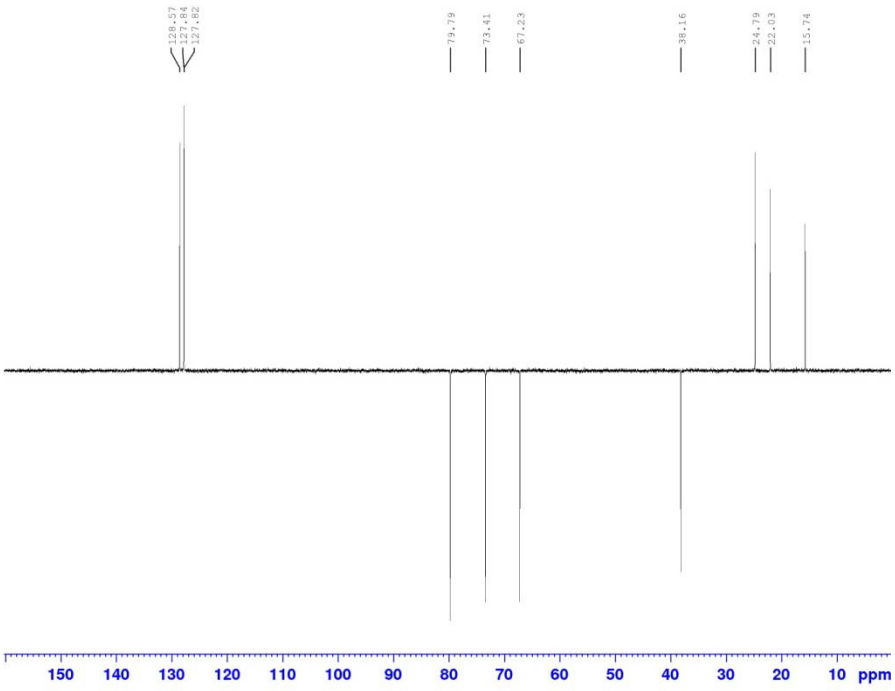


^{13}C NMR

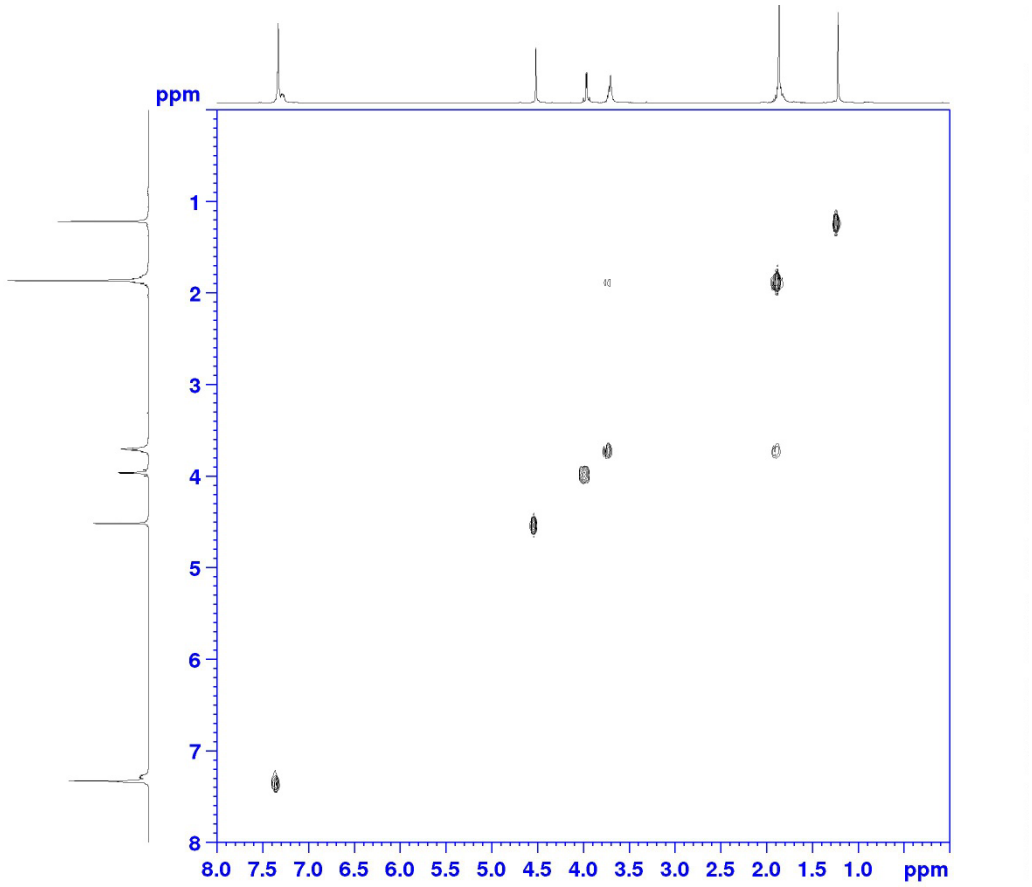


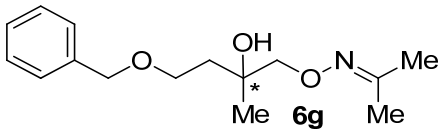


^{13}C DEPT135 NMR

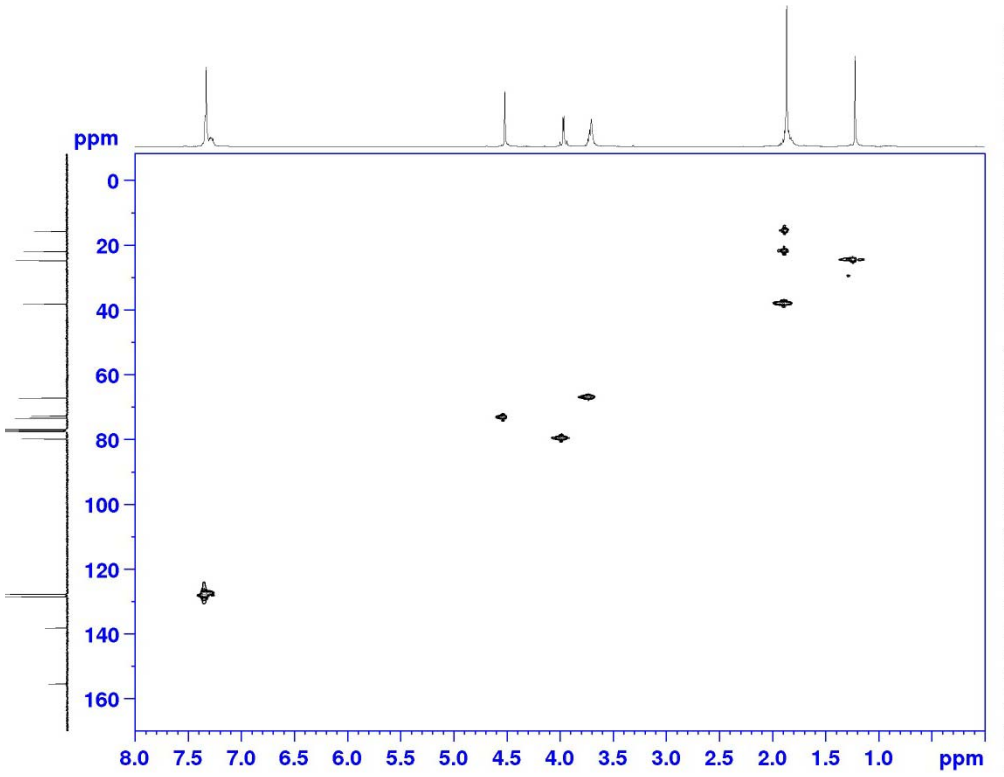


^{1}H-^{1}H COSY

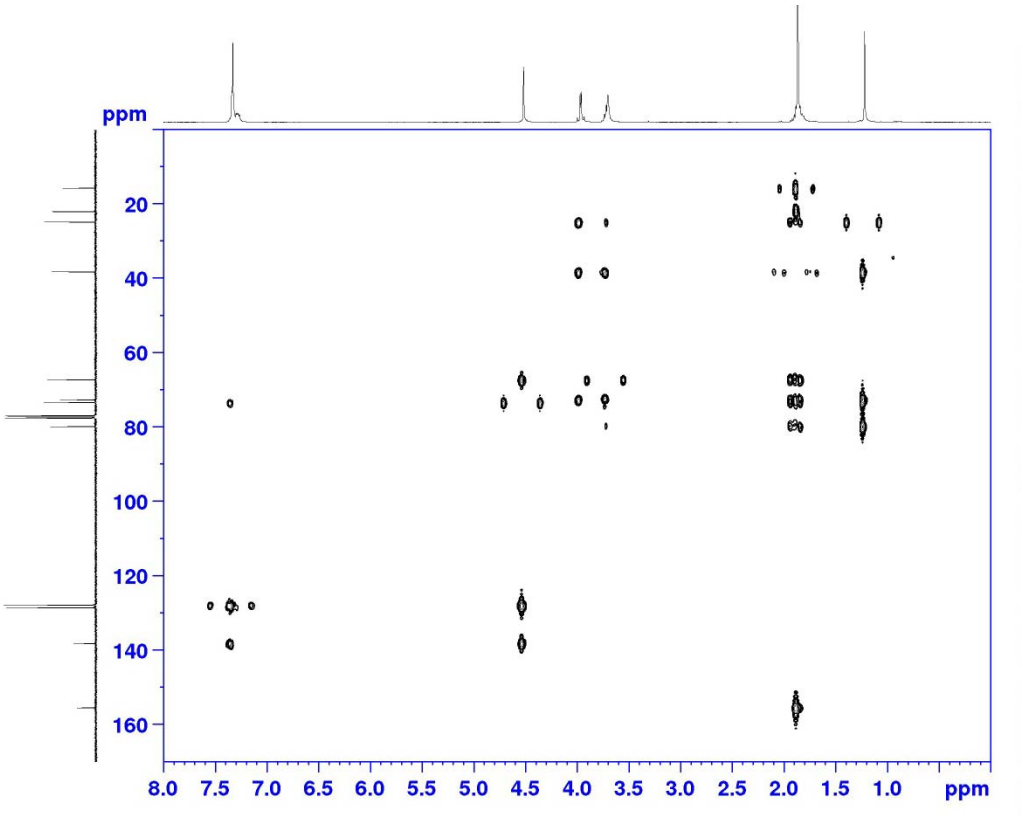


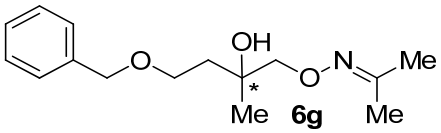


^{1}H-^{13}C HSQC



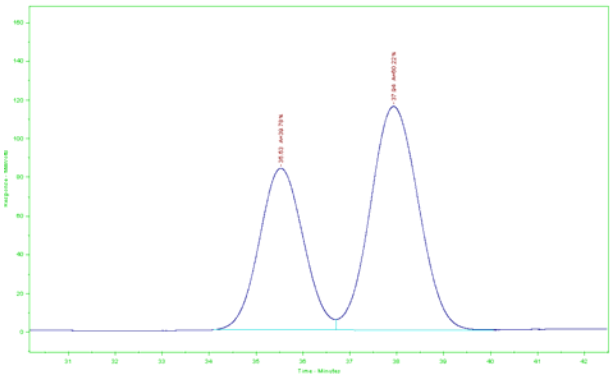
^{1}H-^{13}C HMBC



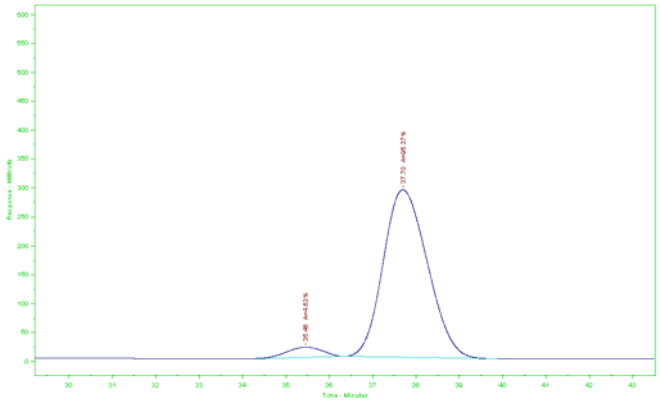


HPLC traces (Chiralpak-IC, 95:5 hexanes:isopropanol @ 1.0 mL/min)

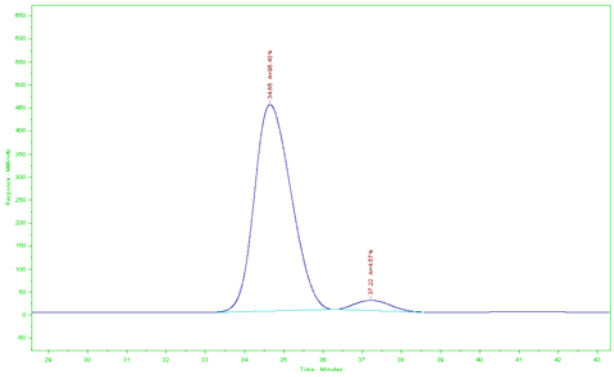
a) racemic mixture



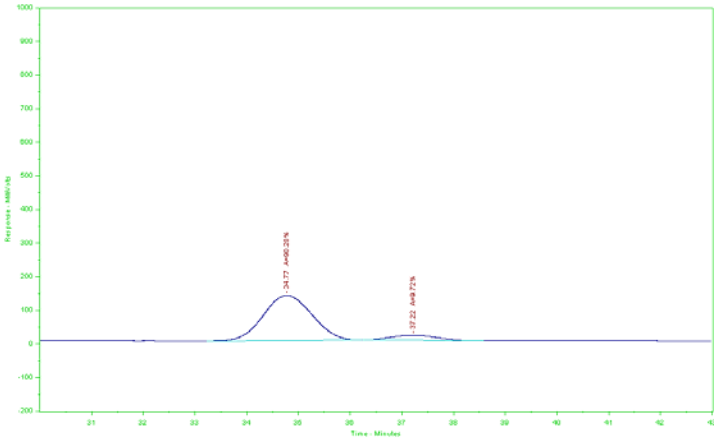
b) *S:R* = 5:95 after CAHB of **5g** with (*R*,*R*)-**L**

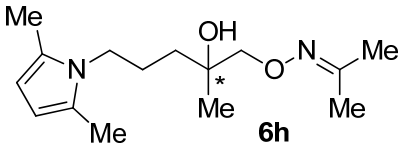


c) *S:R* = 95:5 after CAHB of **5g** with (*S*,*S*)-**L**



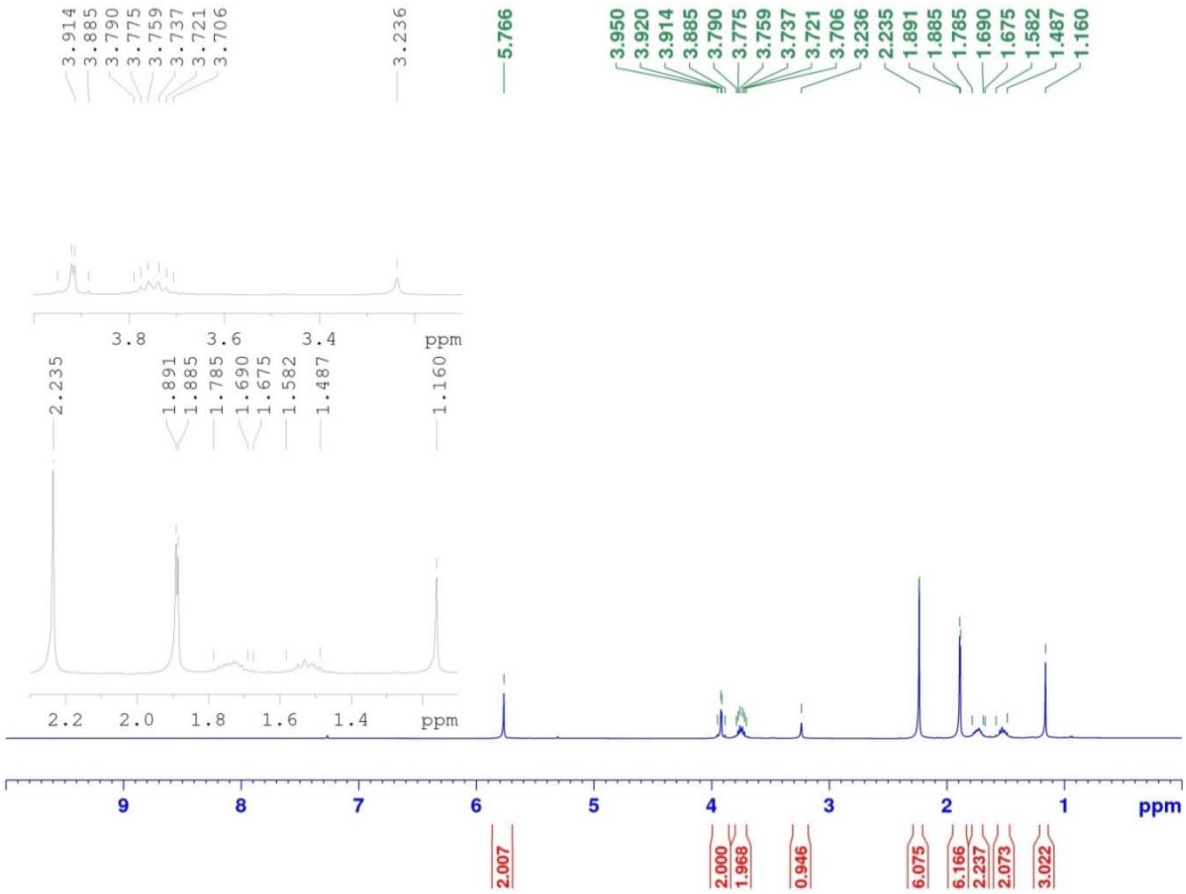
d) *S:R* = 90:10 after CAHB of **10g** and (*R*,*R*)-**L**



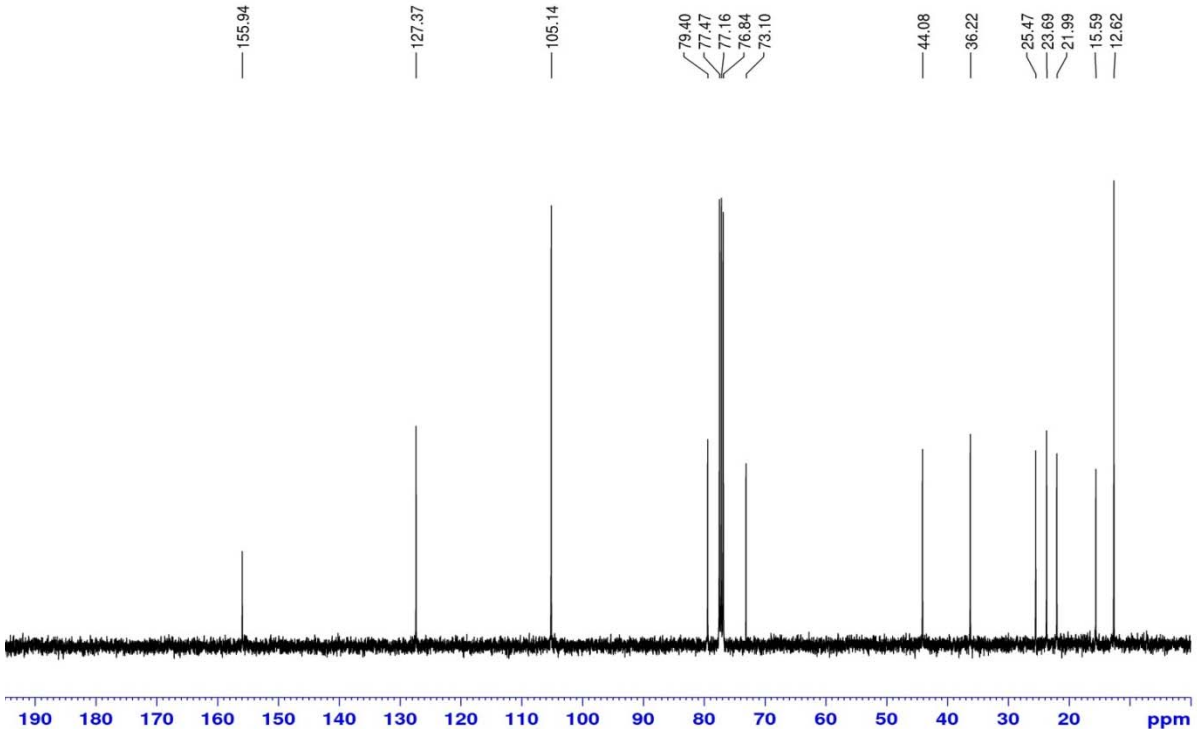


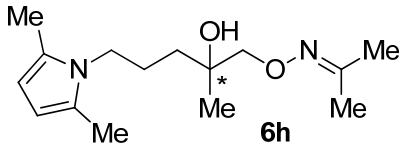
6h

^{1}H NMR



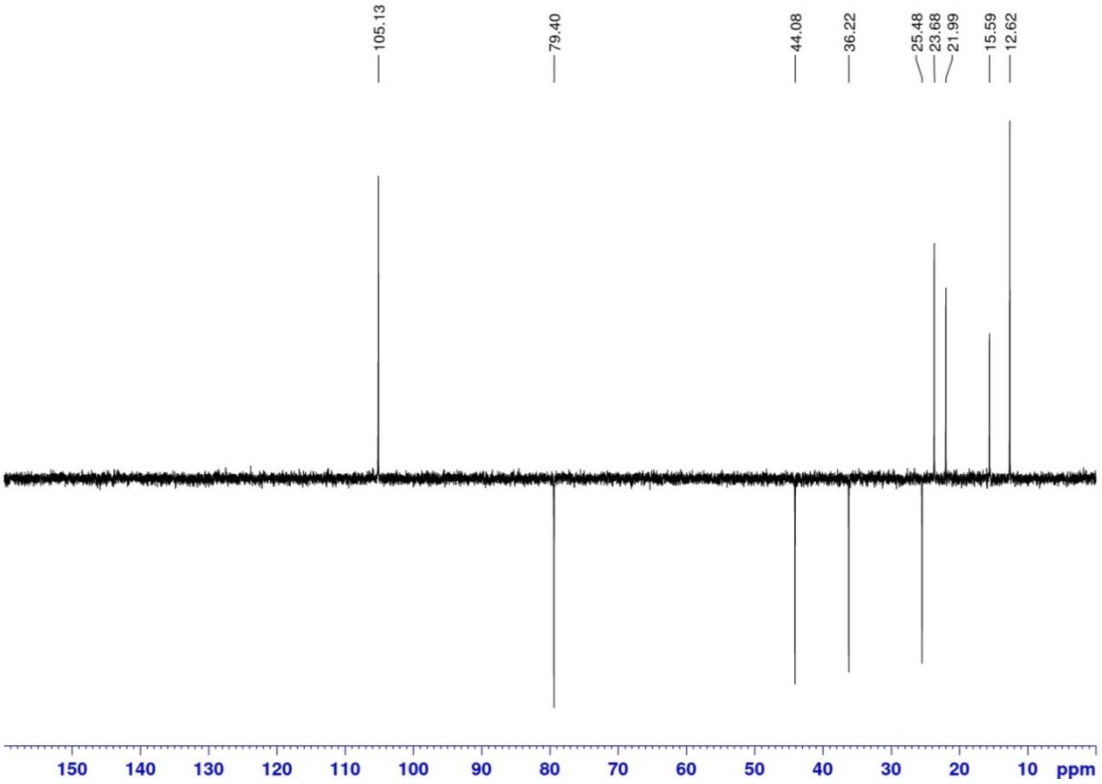
^{13}C NMR



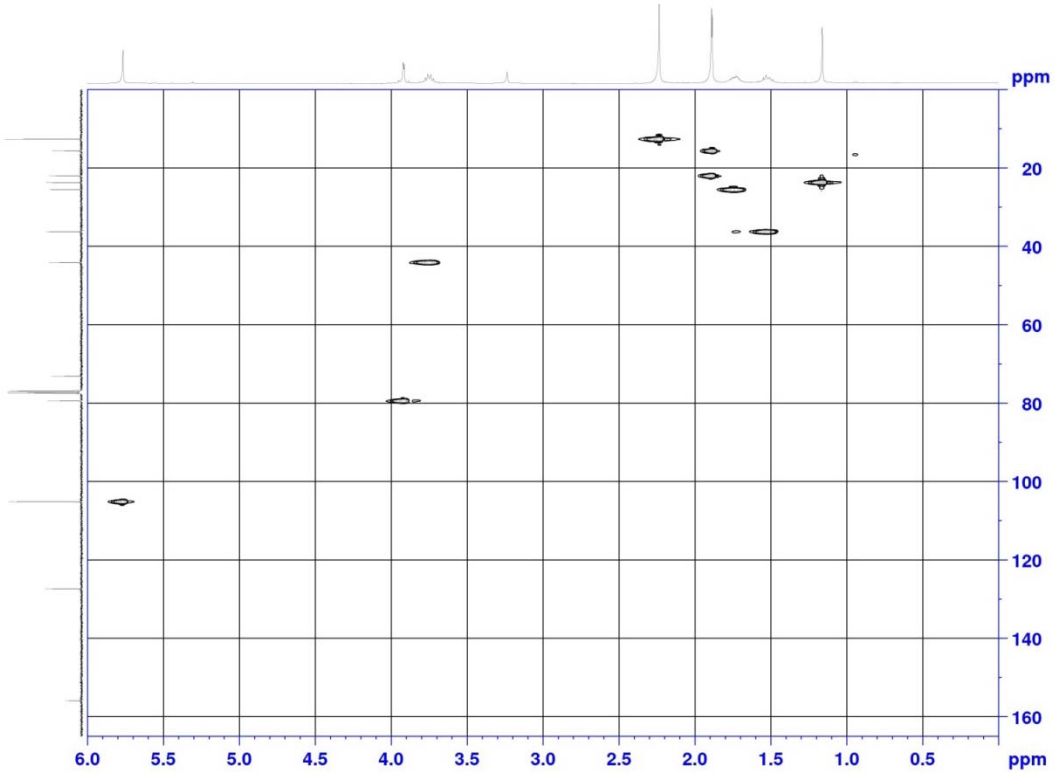


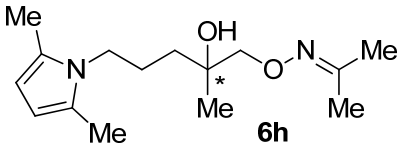
6h

^{13}C DEPT135 NMR



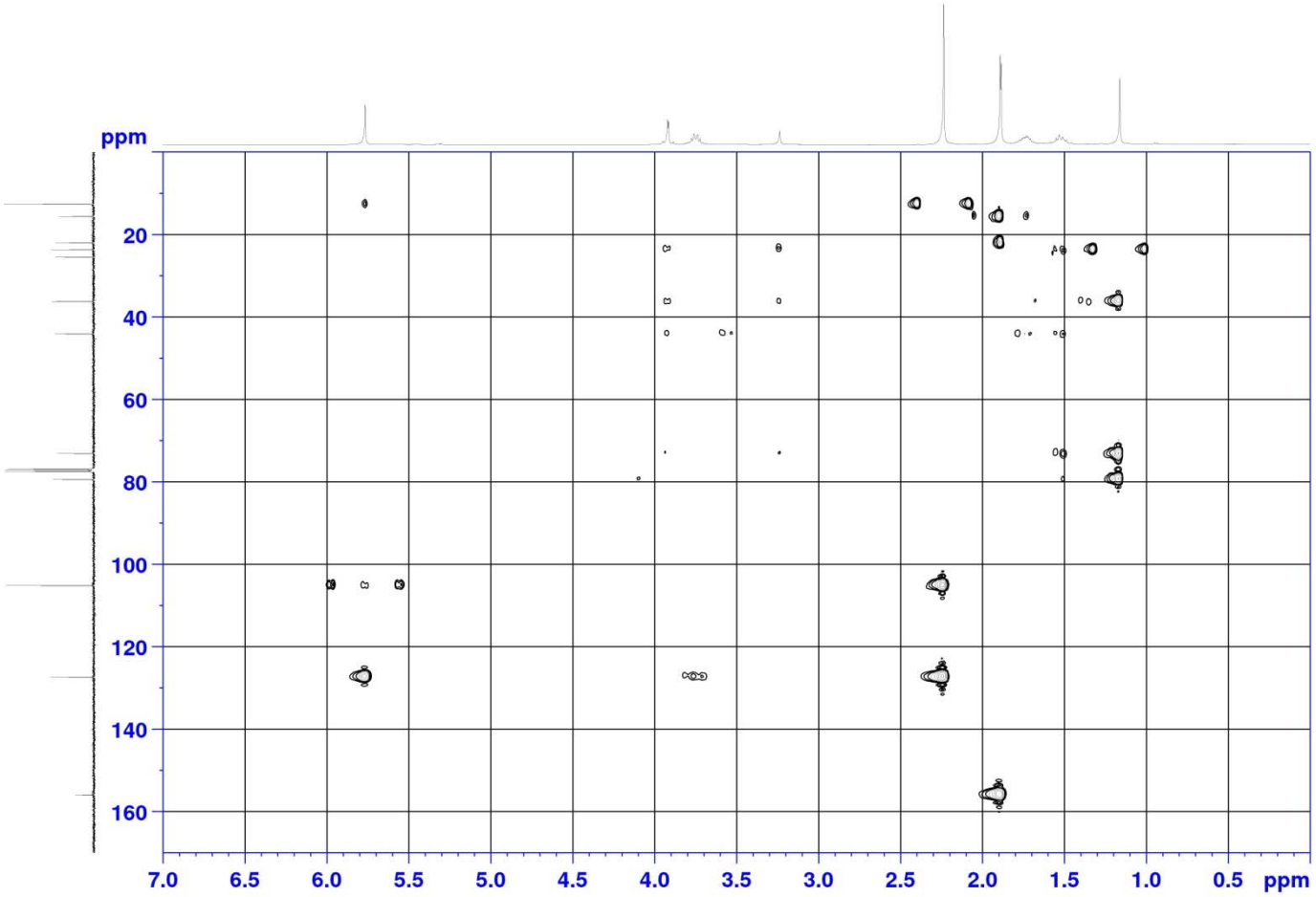
^{1}H-^{13}C HSQC





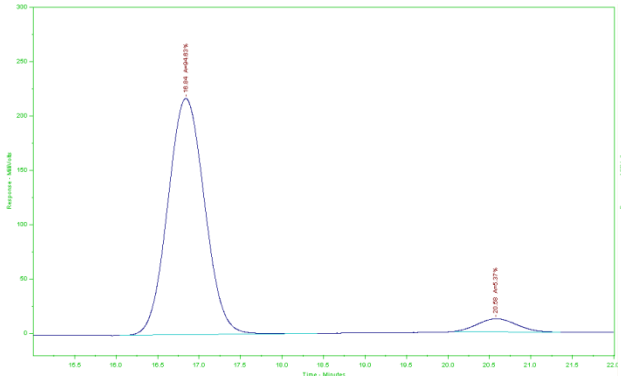
6h

^{1}H-^{13}C HMBC

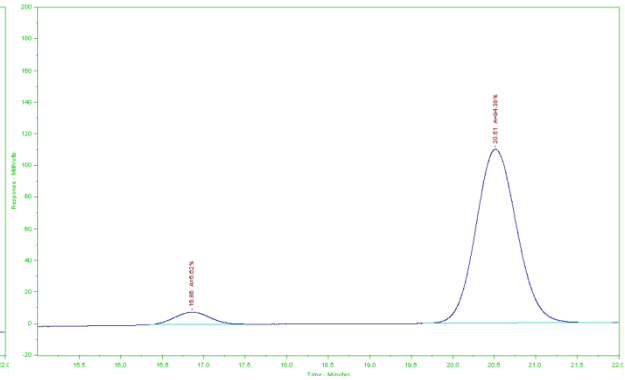


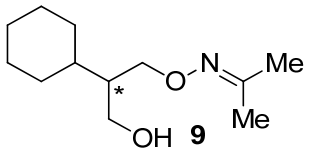
HPLC traces (Chiralpak IC, 90:10 hexanes:isopropanol @ 1.0 mL/min) for

a) *R*:*S* = 95:5 after **5h** and (*R*,*R*)-**L**



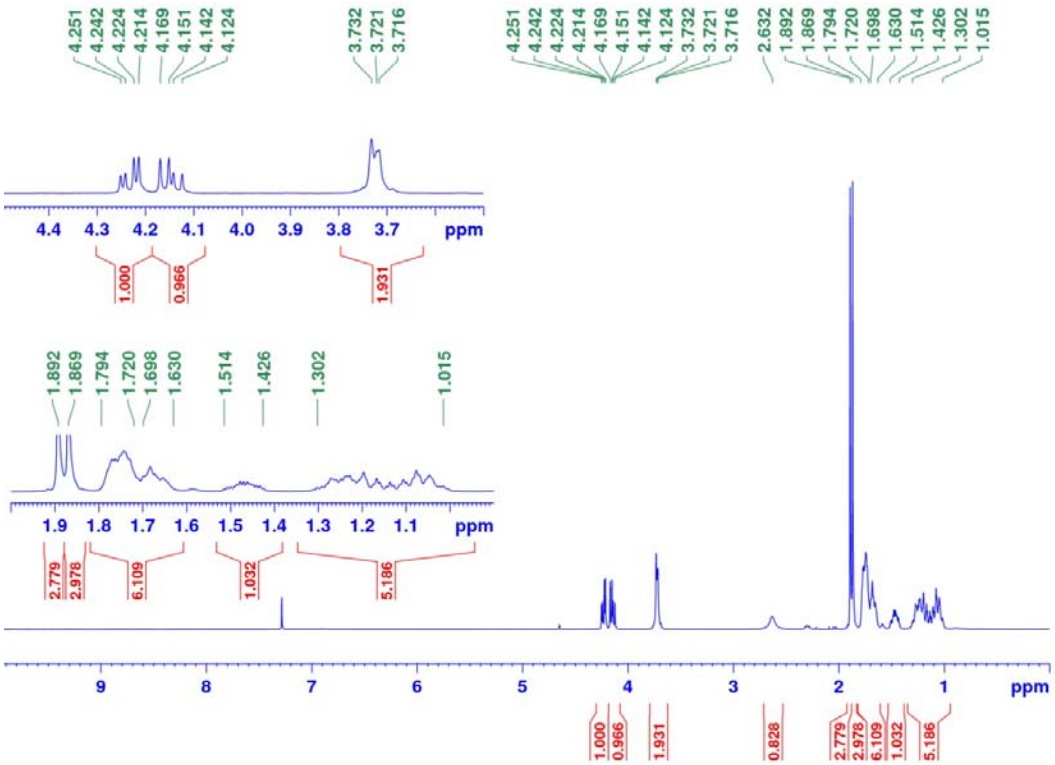
b) *R*:*S* = 6:94 after **10h** and (*R*,*R*)-**L**



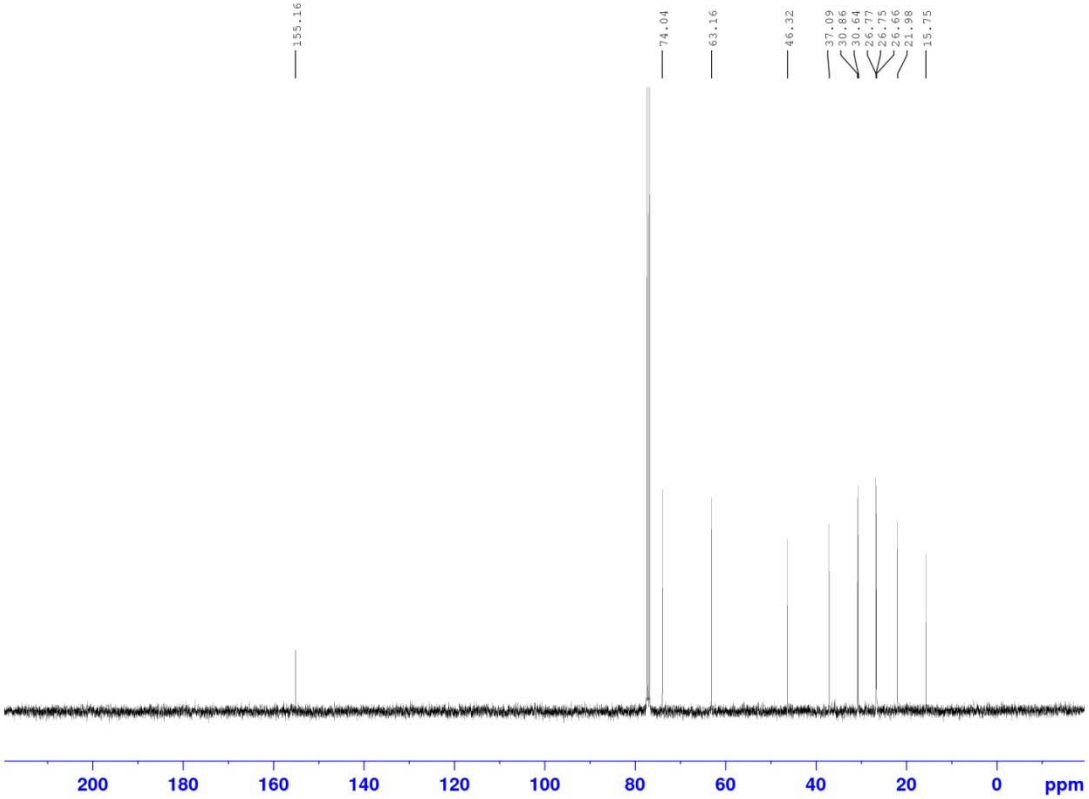


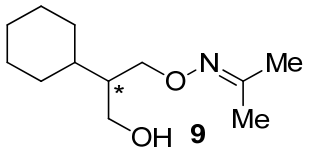
9

^{1}H NMR



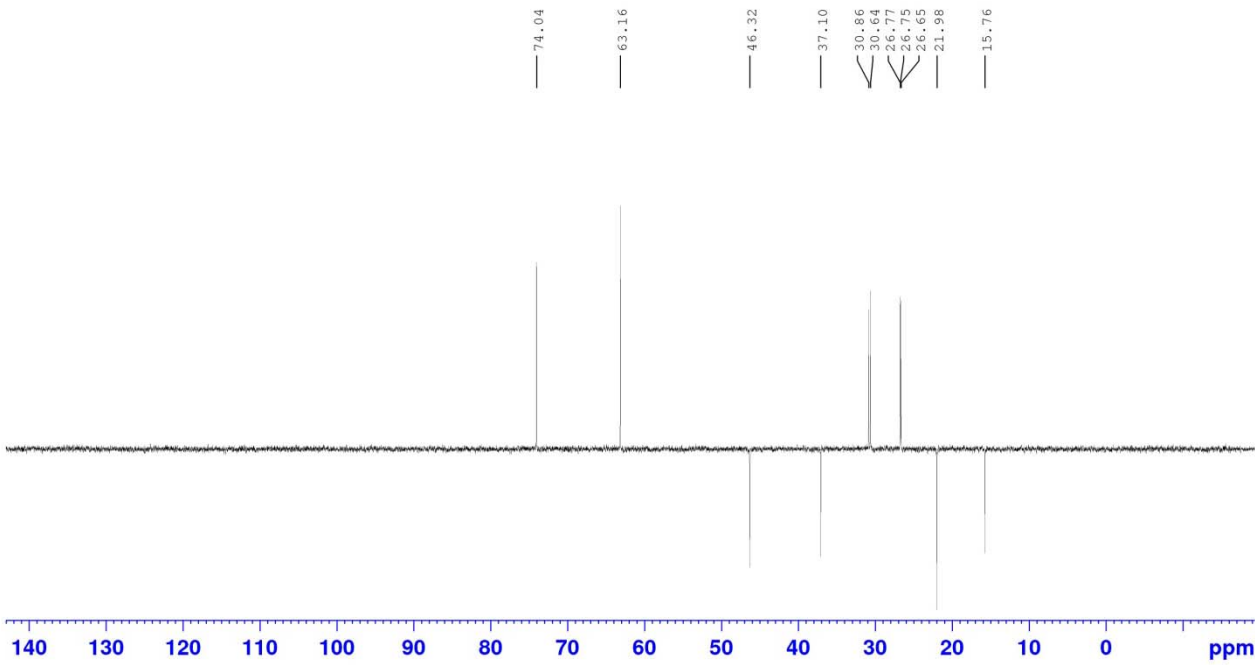
^{13}C NMR



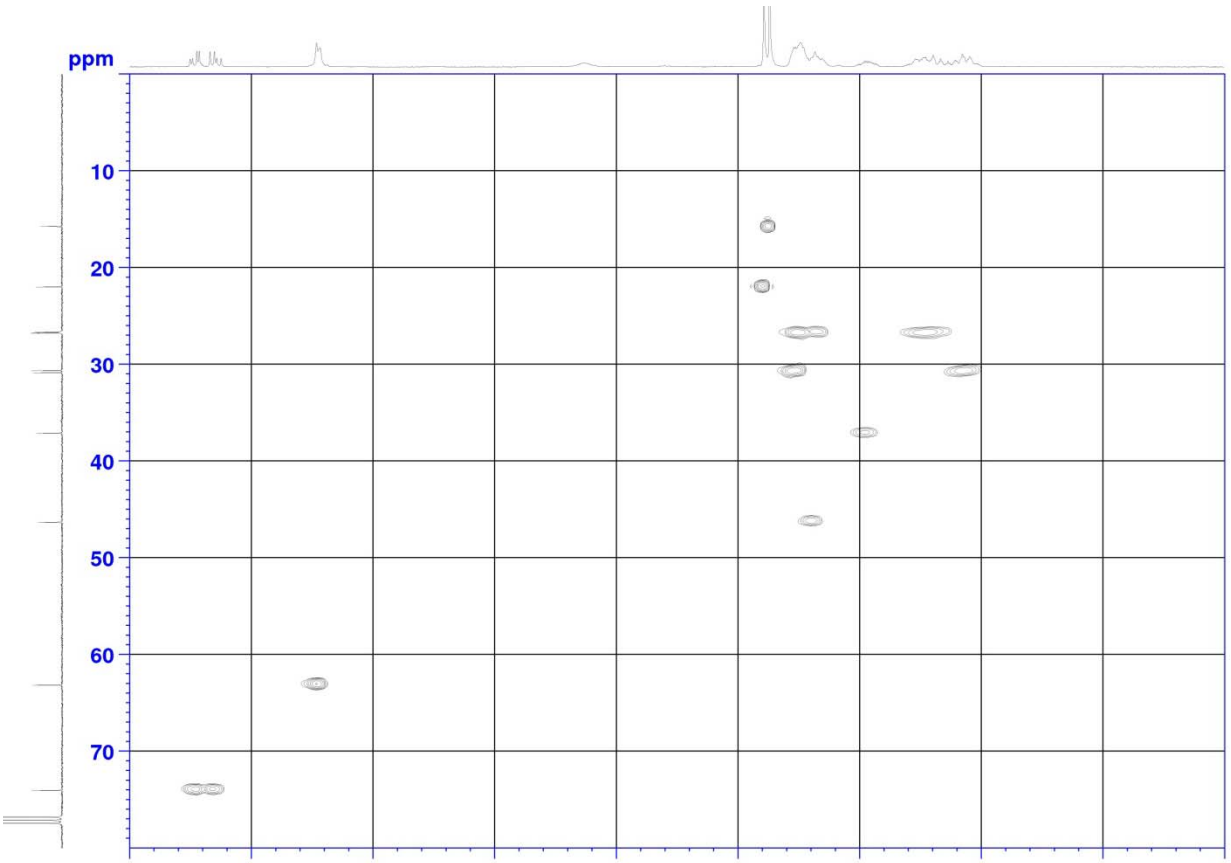


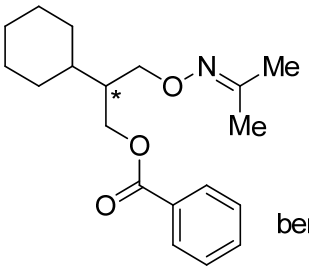
9

^{13}C DEPT NMR



^{1}H -^{13}C HSQC NMR

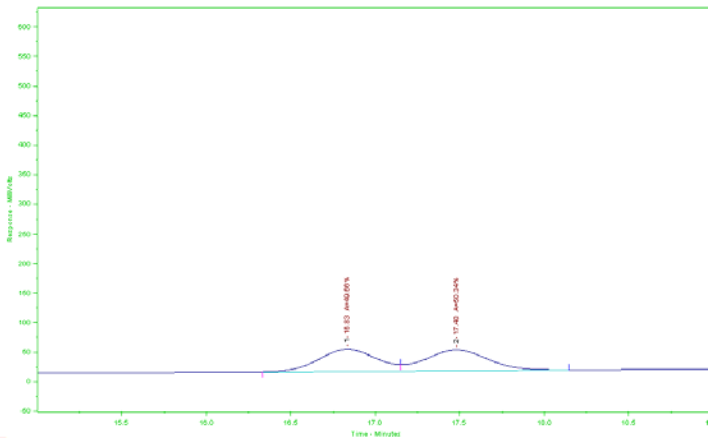




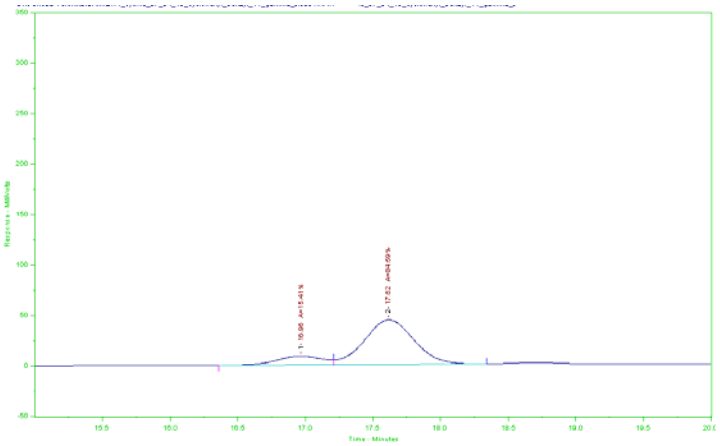
benzyl ester of **9**

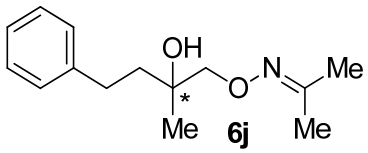
HPLC traces (Chiralpak-IC 95:5 hexanes:isopropanol @ 1.0 mL/min)

a) racemic mixture



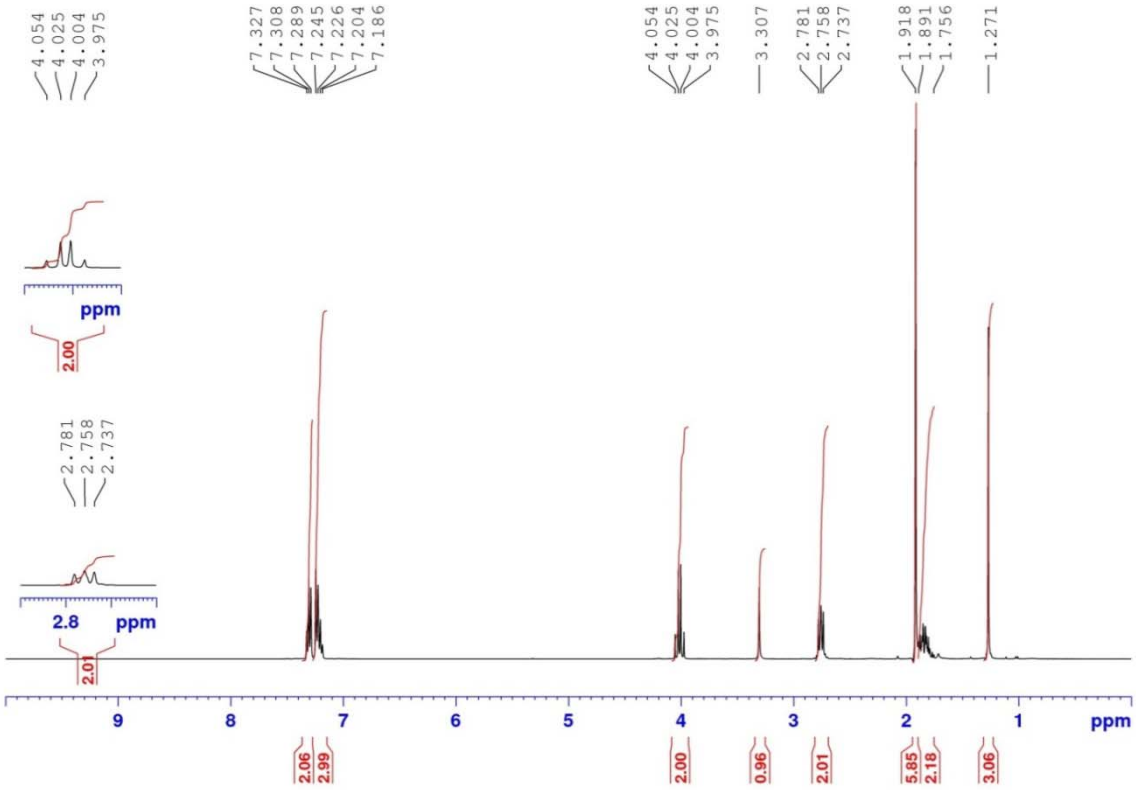
b) after CAHB of **5i** with (*S*,*S*)-**L**



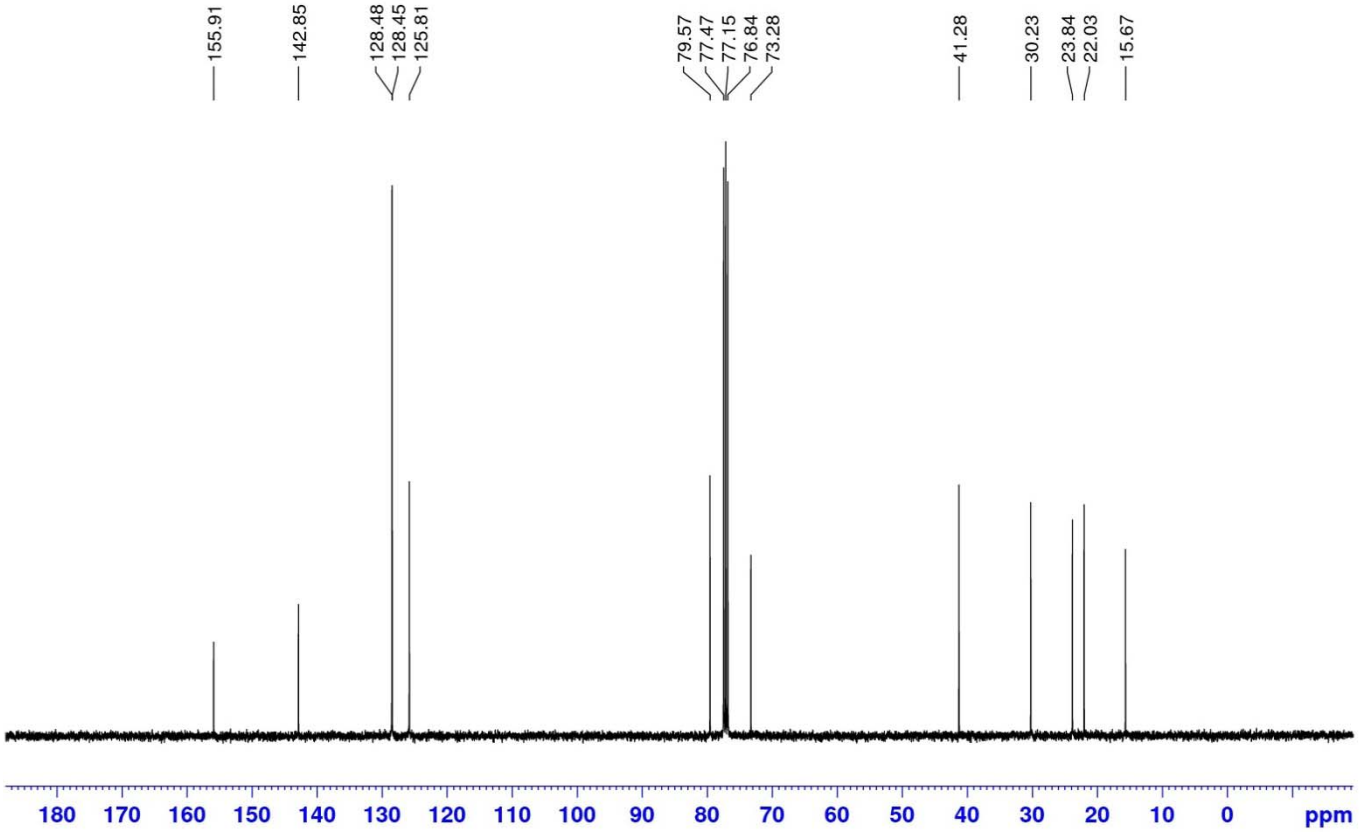


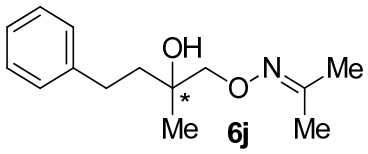
6j

^{1}H NMR

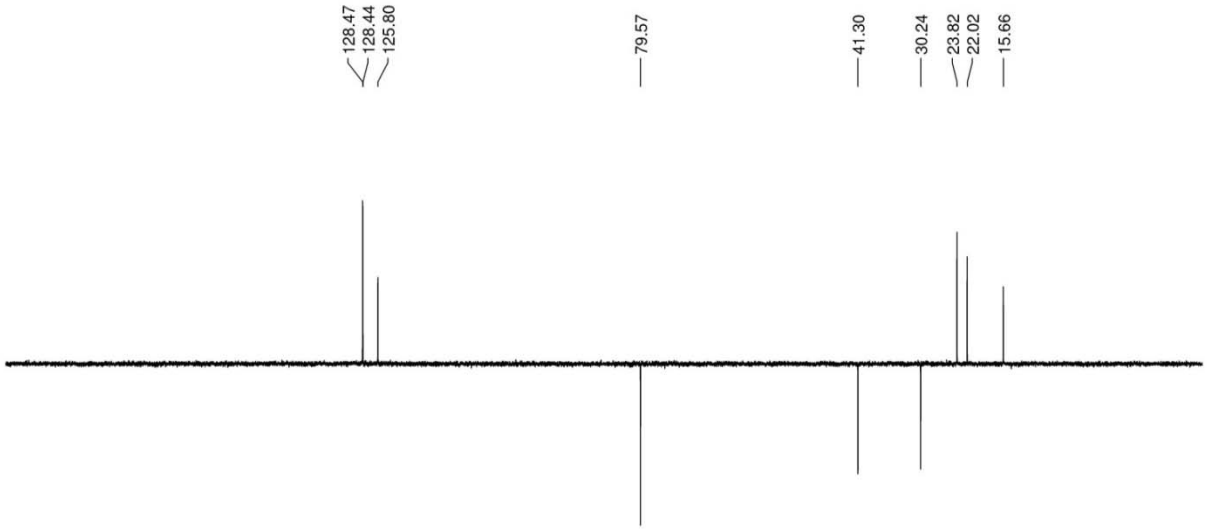


^{13}C NMR

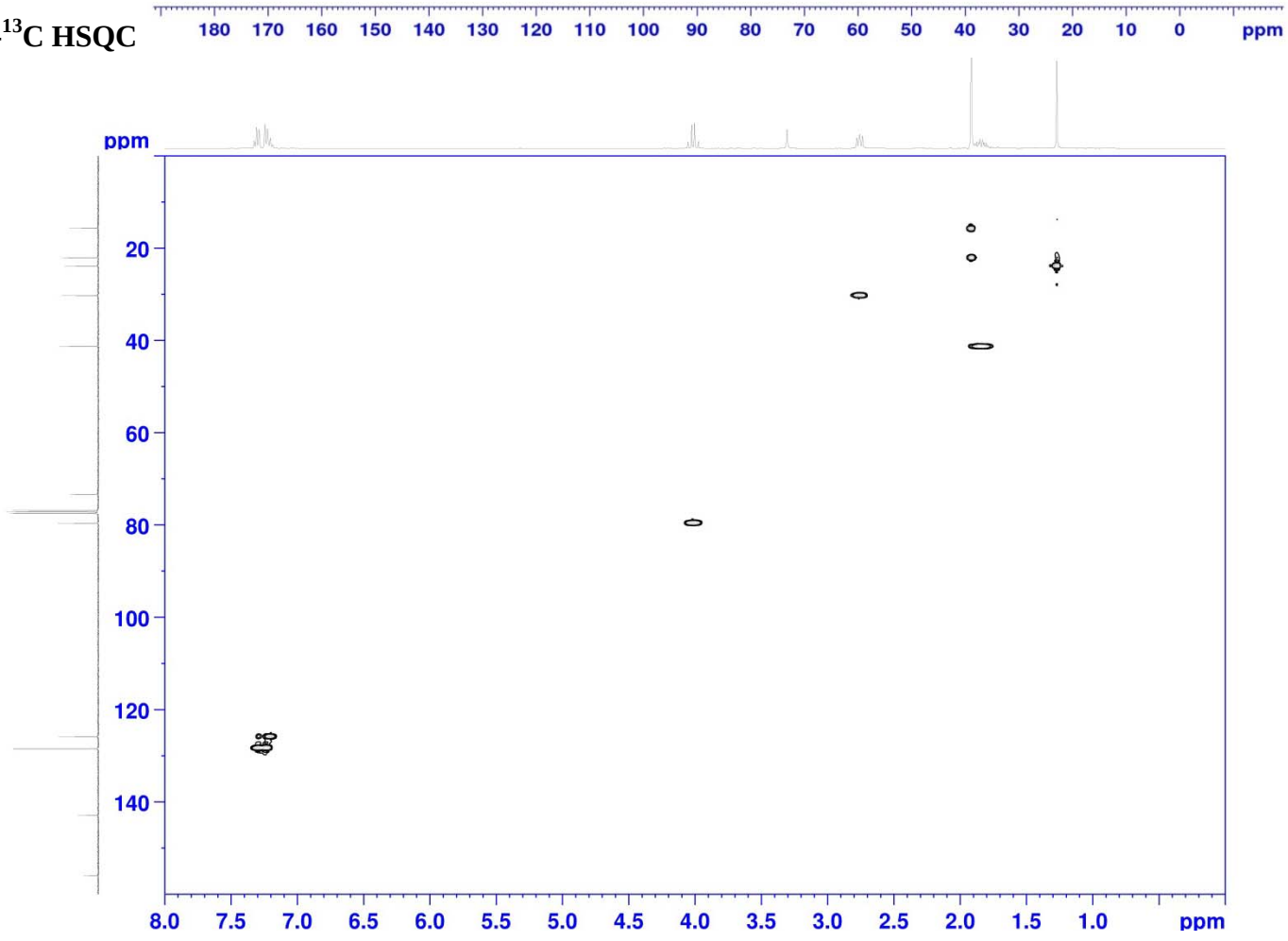


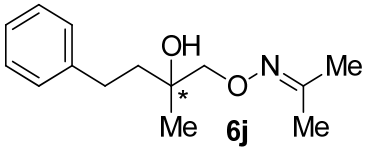


^{13}C DEPT135 NMR



^{1}H-^{13}C HSQC

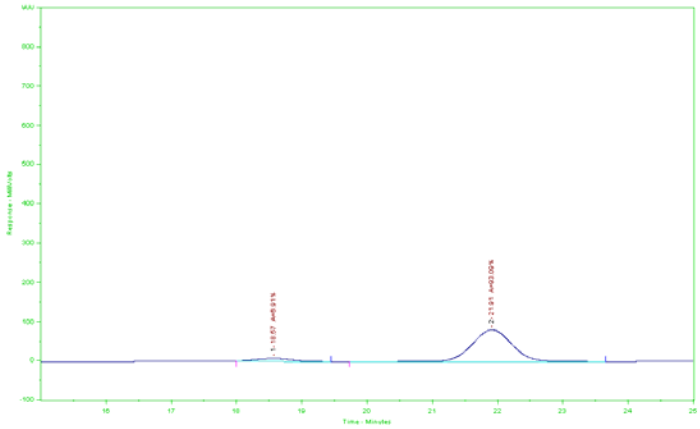




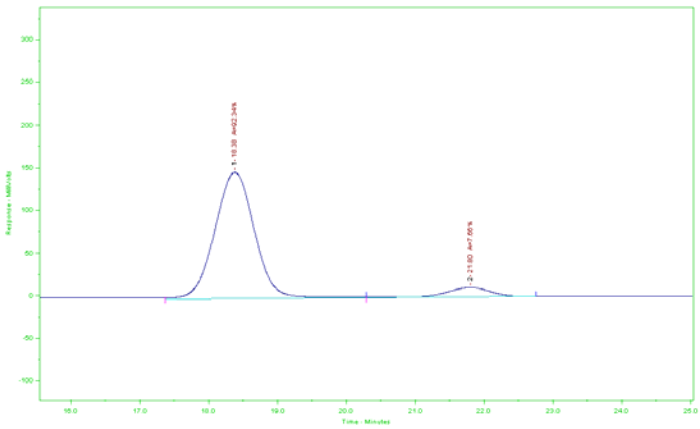
6j

HPLC traces (Chiralpak-IB, 97:3 hexanes:isopropanol @ 1.0 mL/min)

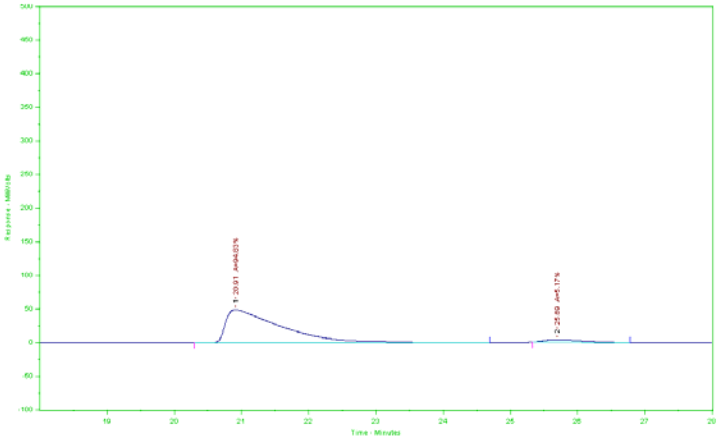
a) *S*:*R* = 7:93 after CAHB of **5j** with (*R*,*R*)-**L**



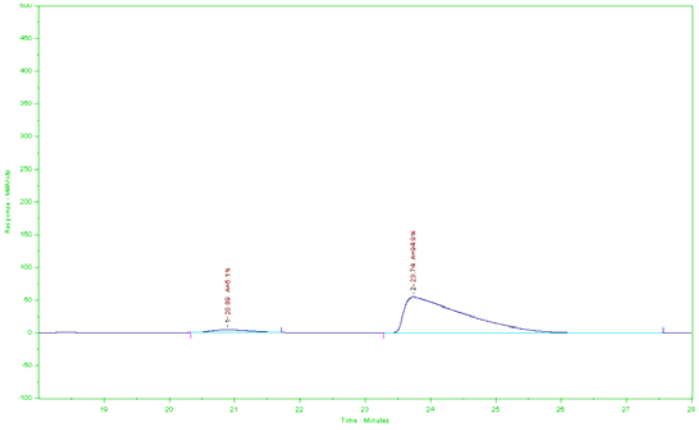
b) *S*:*R* = 92:8 after CAHB of **5j** with (*S*,*S*)-**L**

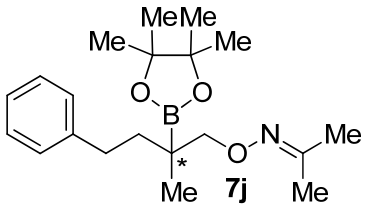


c) *S*:*R* = 94:6 after CAHB of **10j** with (*R*,*R*)-**L**

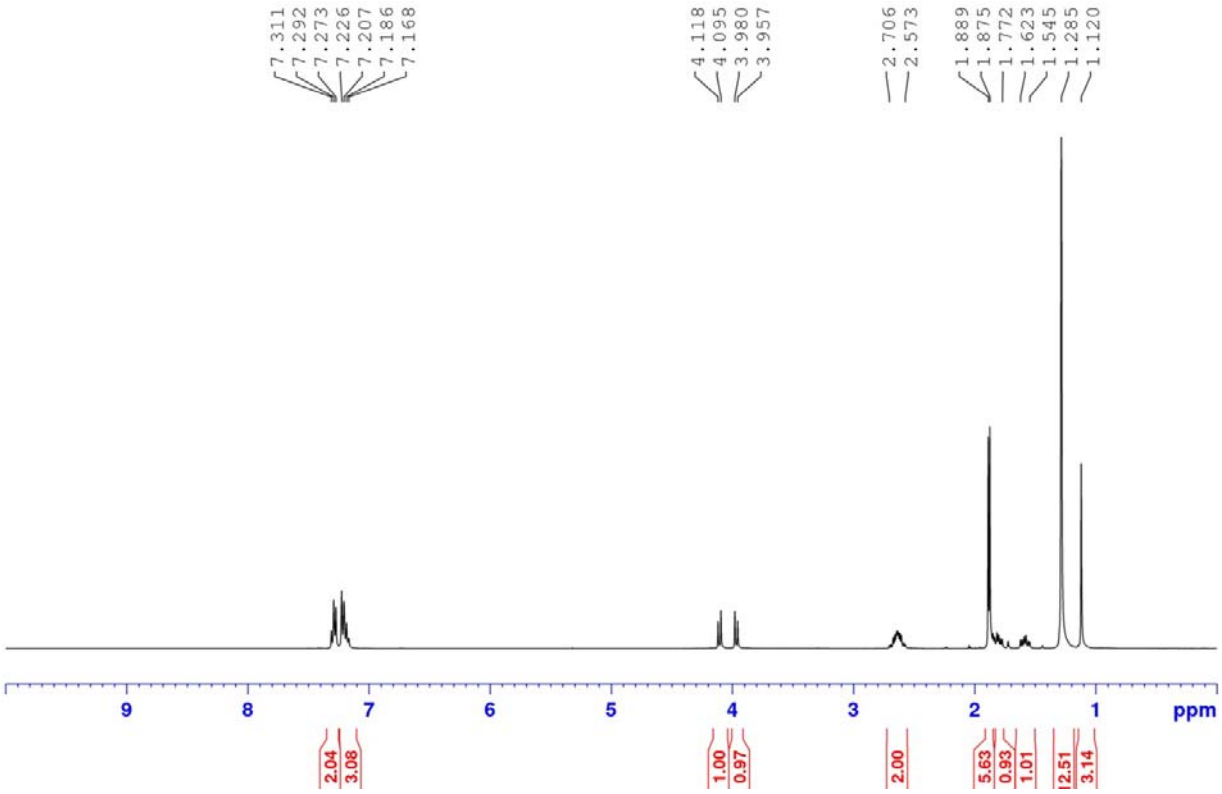


d) *S*:*R* = 5:95 after CAHB of **10j** with (*S*,*S*)-**L**

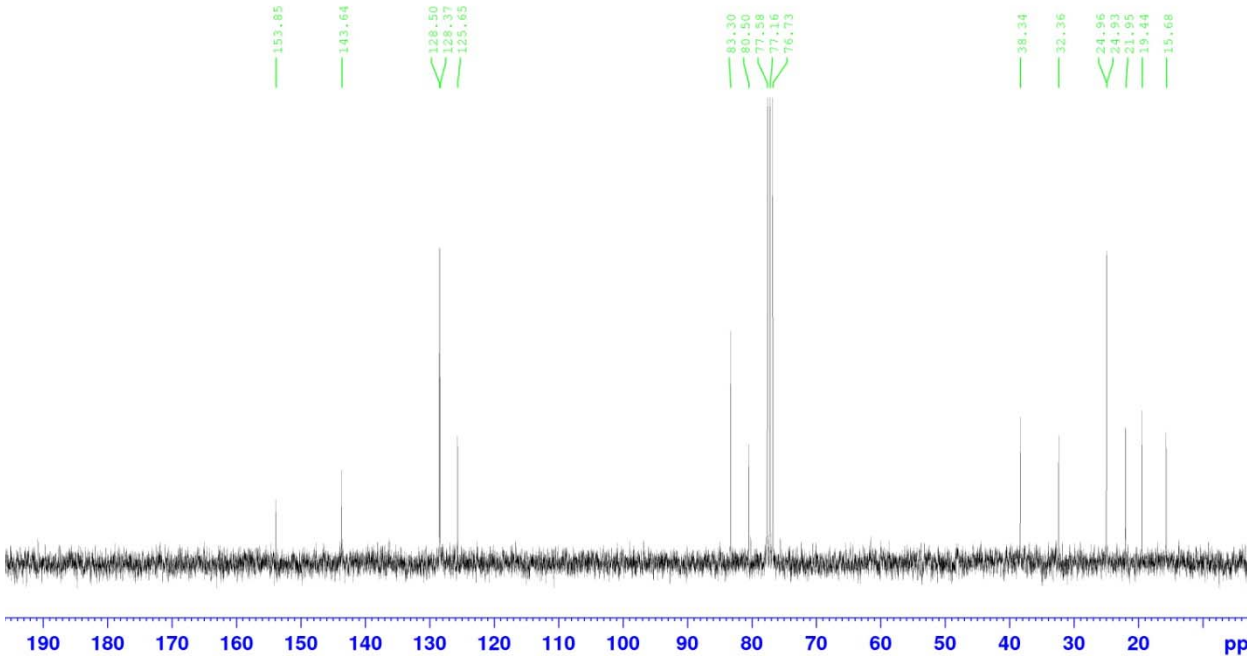


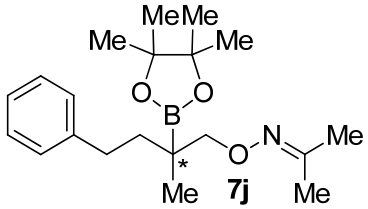


^{1}H NMR

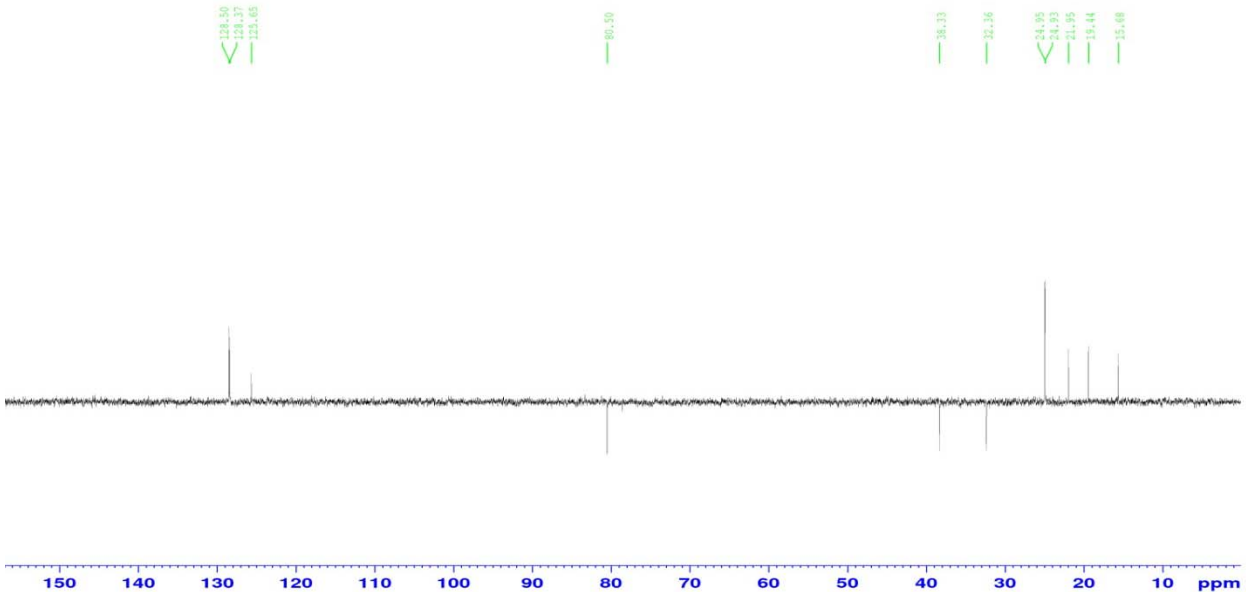


^{13}C NMR

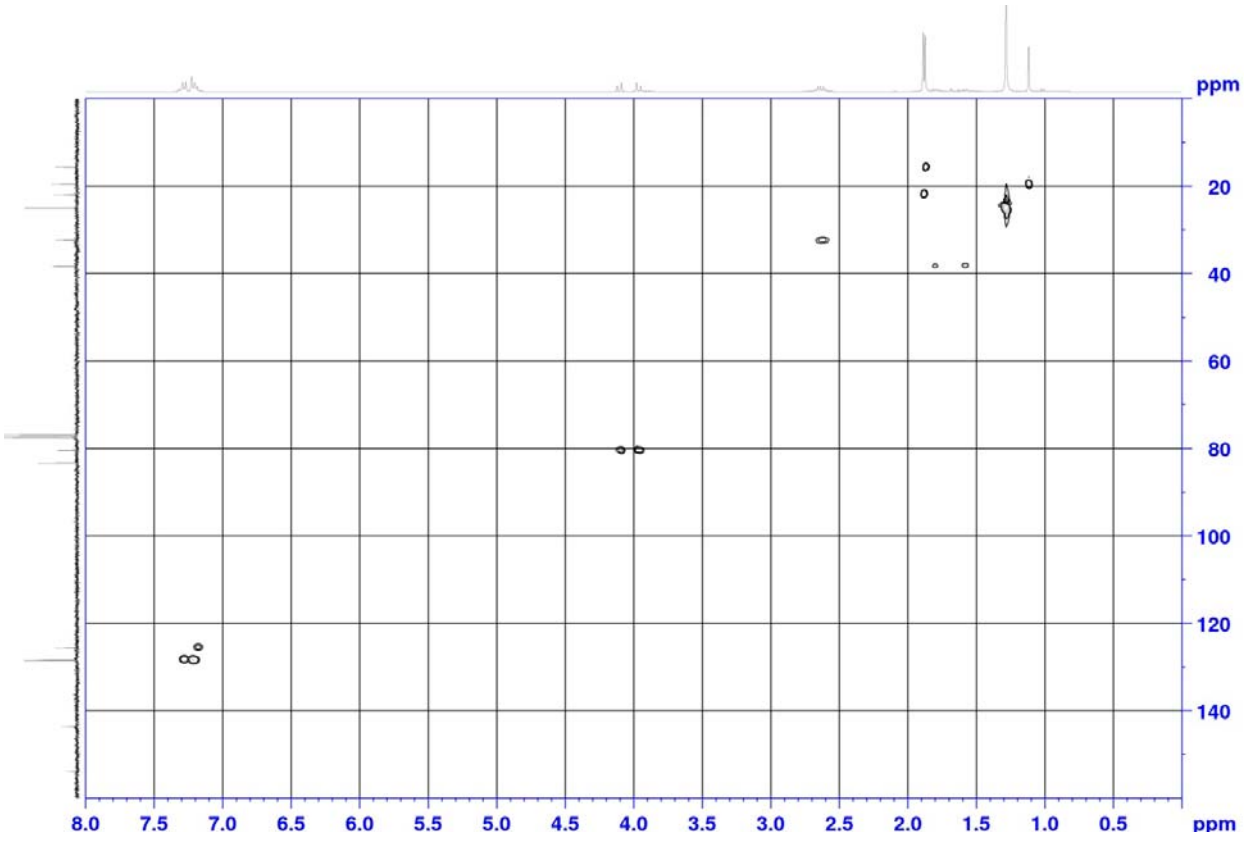


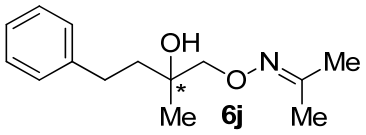


^{13}C DEPT 135 NMR



^{1}H-^{13}C HSQC

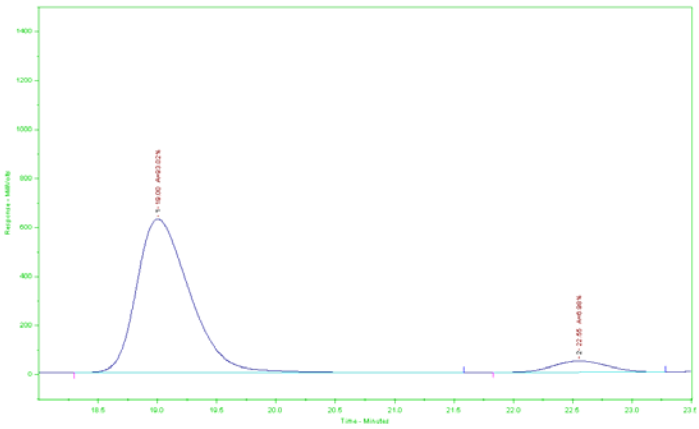




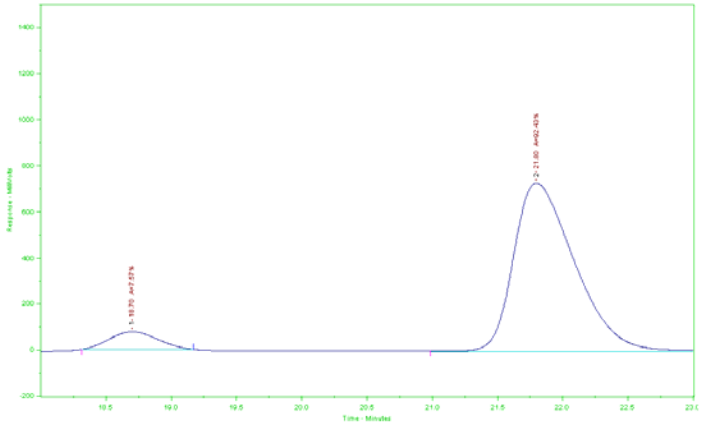
6j

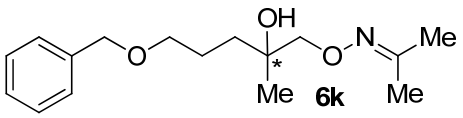
HPLC traces (Chiralpak-IB, 97:3 hexanes:isopropanol @ 1.0 mL/min)

a) *S:R* = 93:7 after C-B bond cleavage of (*S*)-**7j**

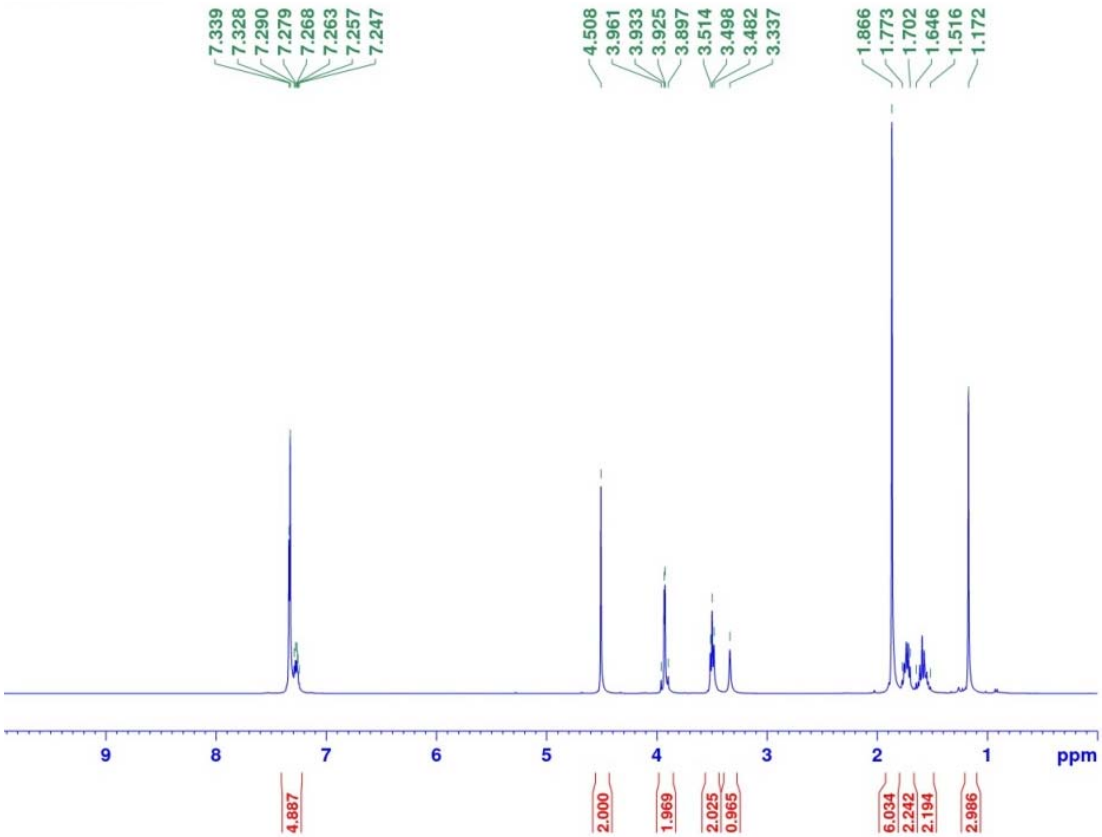


b) *S:R* = 8:92 after C-B bond cleavage of (*R*)-**7j**

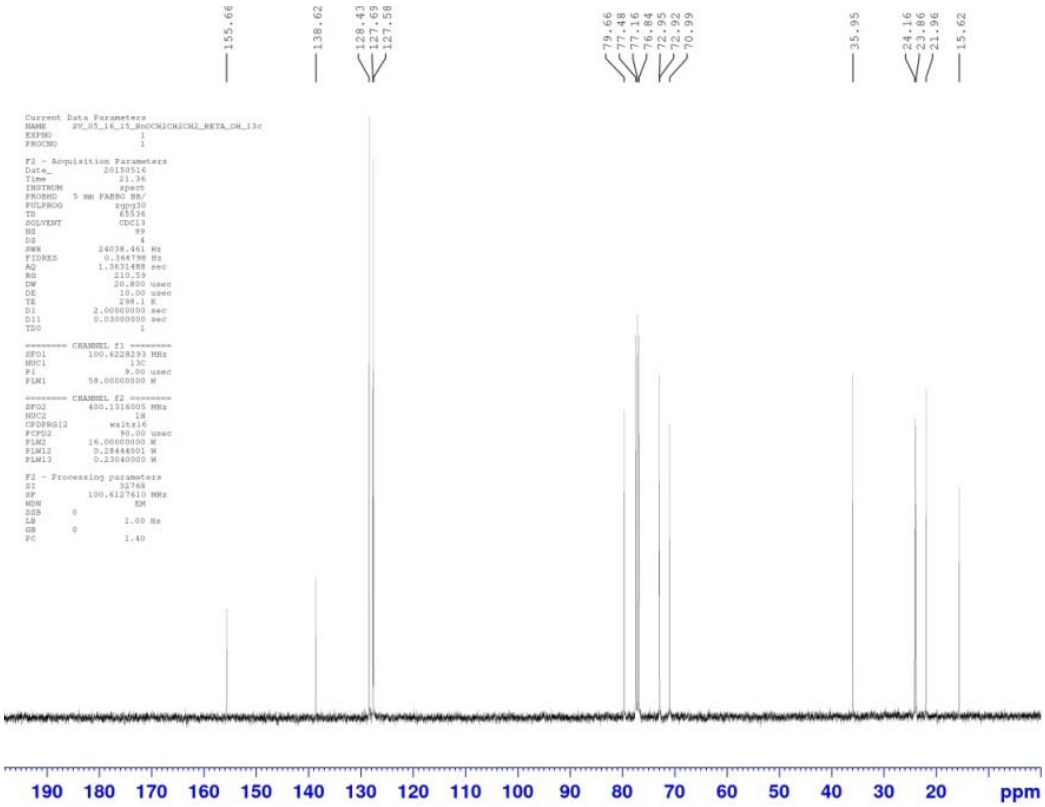




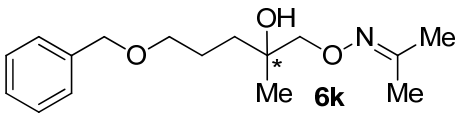
^{1}H NMR

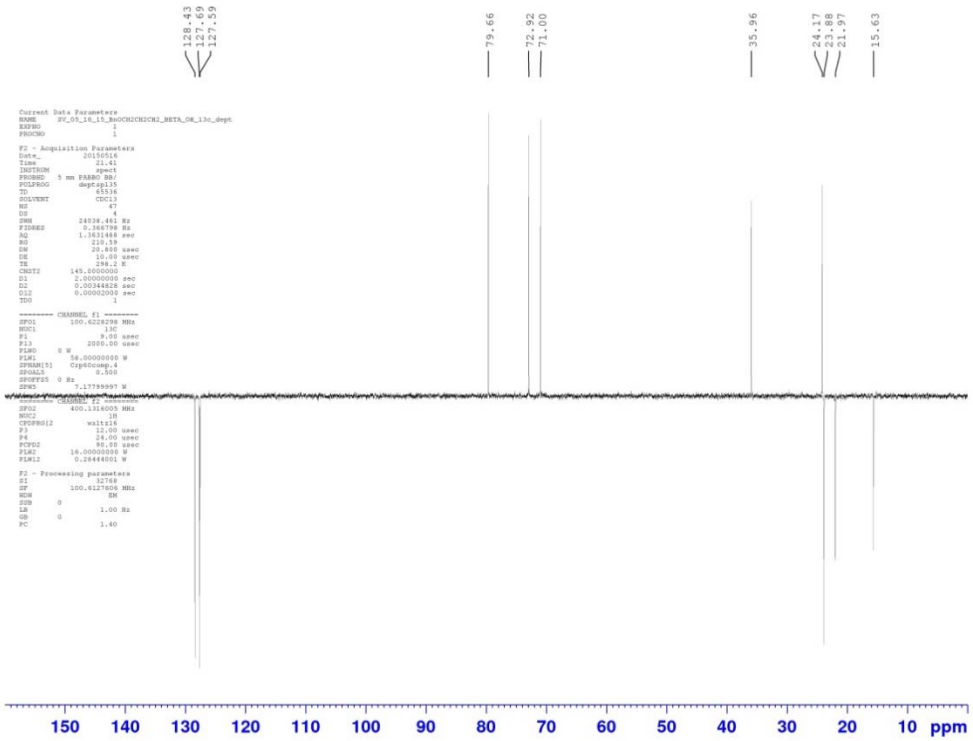


^{13}C NMR

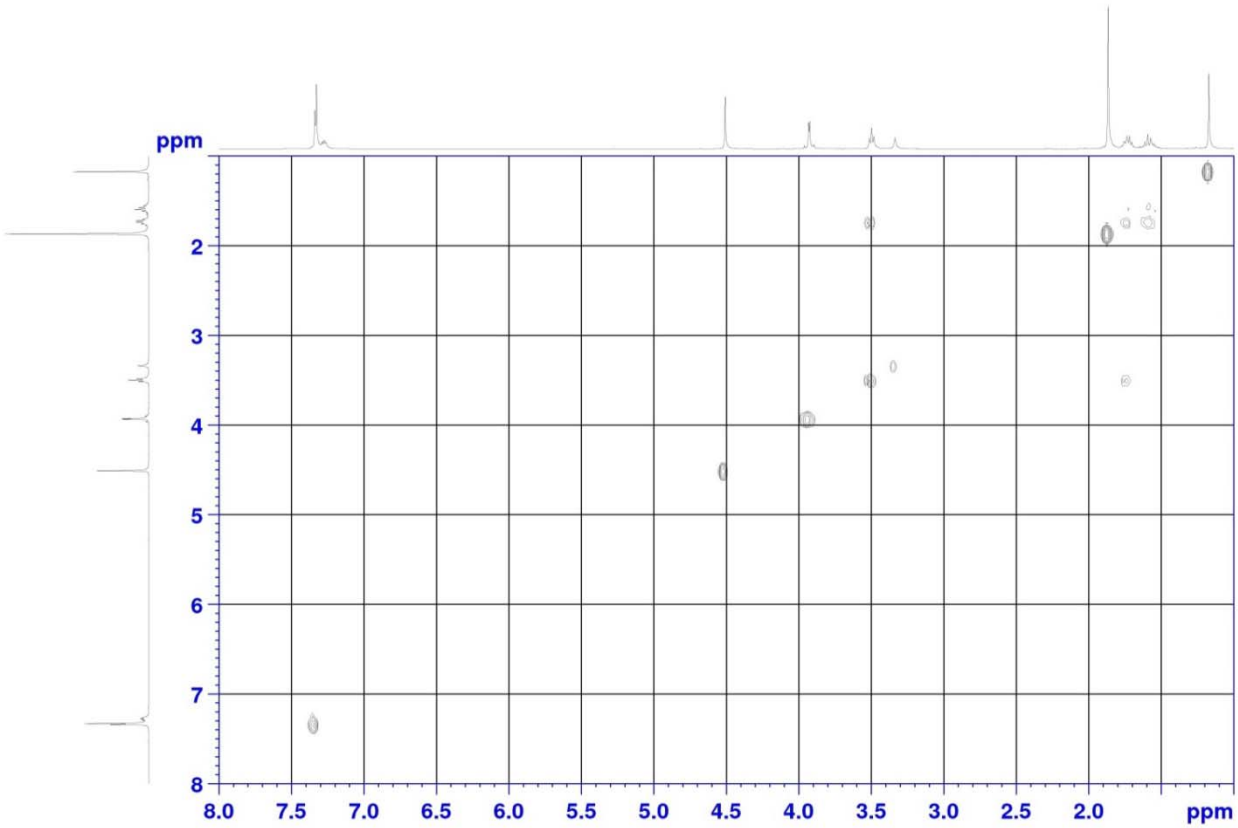


^{13}C DEPT135 NMR

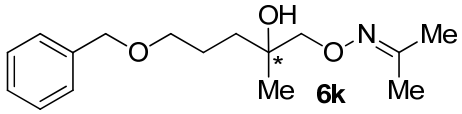


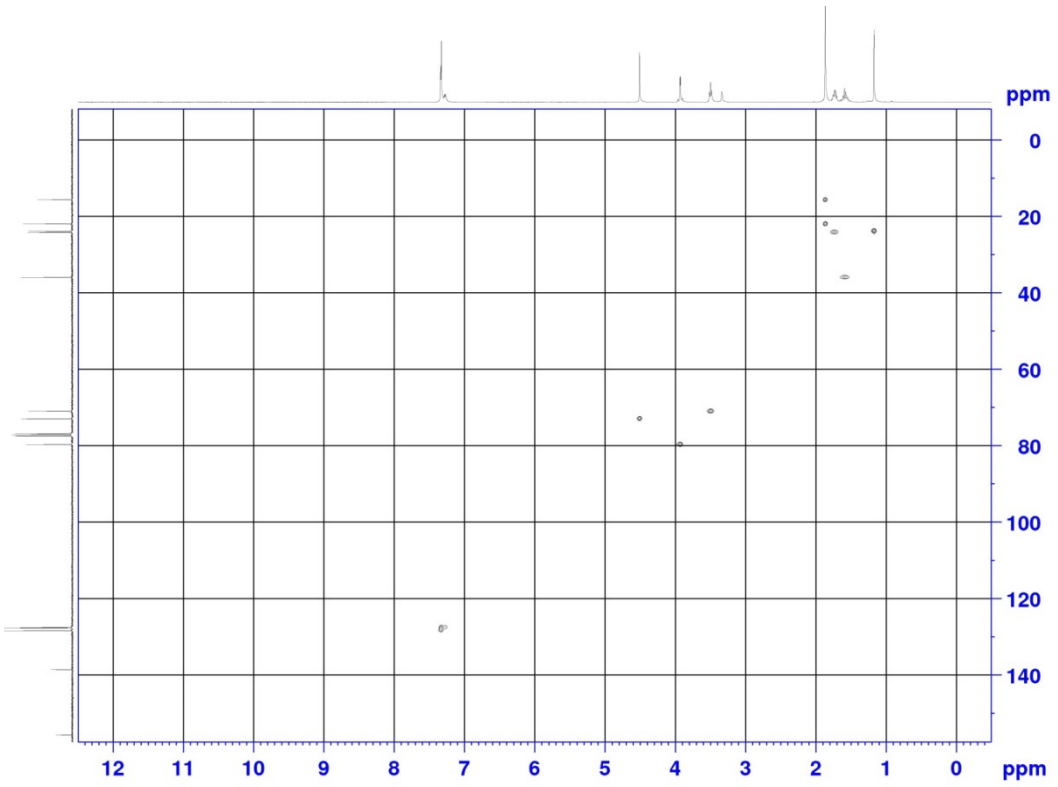


^{1}H-^{1}H COSY NMR

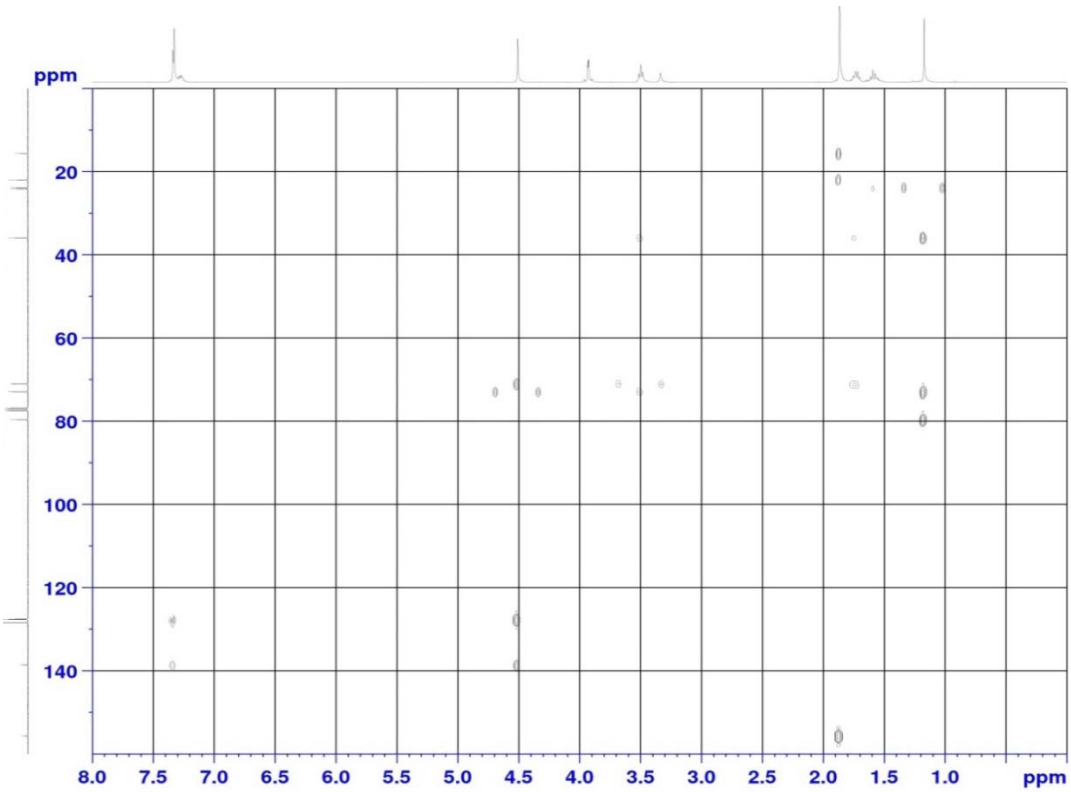


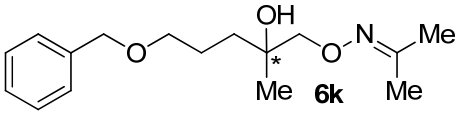
^{1}H-^{13}C HSQC NMR





^{1}H-^{13}C HMBC NMR

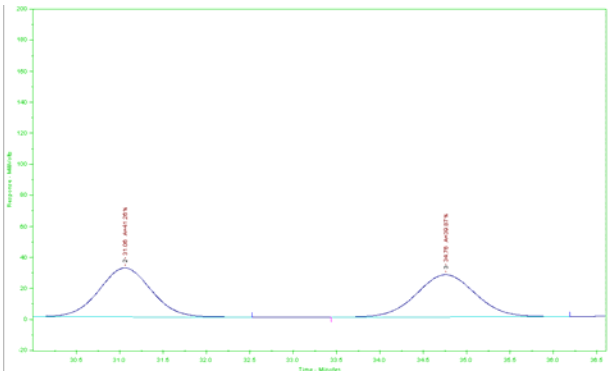




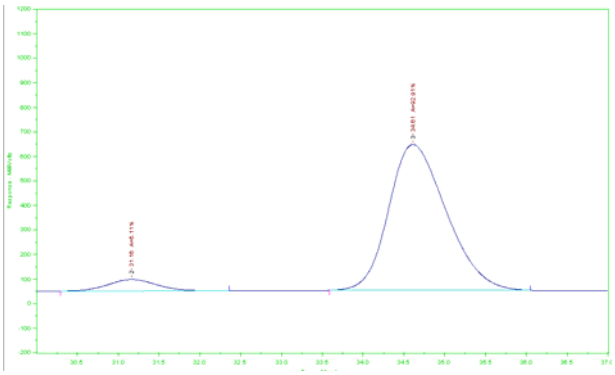
6k

HPLC traces (Chiralpak-IC, 90:10 hexanes:isopropanol @ 1.0 mL/min) for

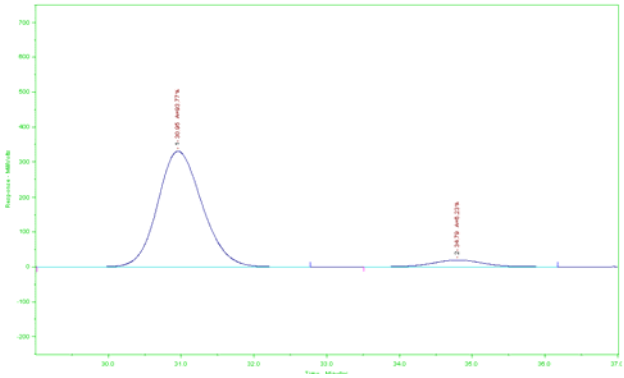
a) racemic mixture

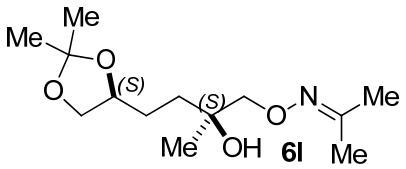


b) *R*:*S* = 6:94 after CAHB of **10k** with (*R*,*R*)-**L**



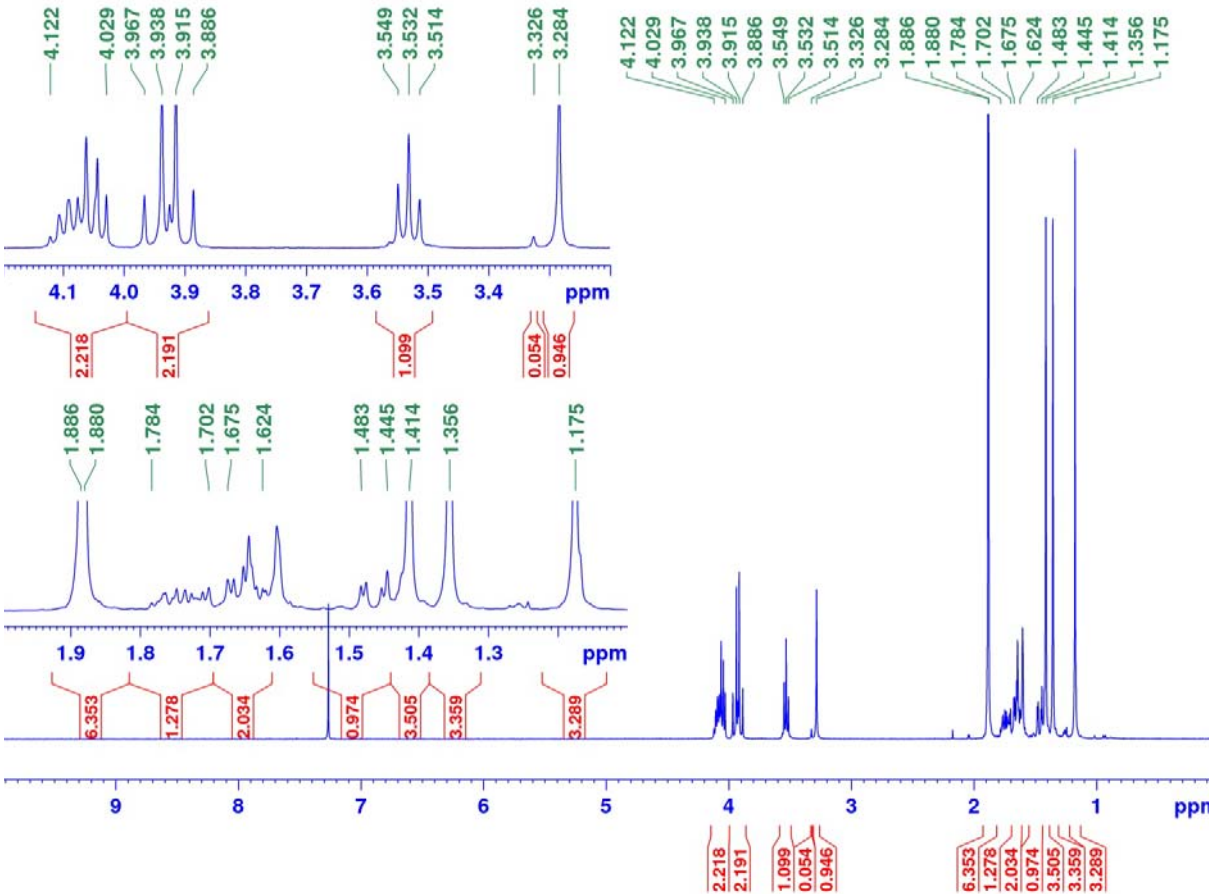
c) *R*:*S* = 94:6 after CAHB of **10k** with (*S*,*S*)-**L**



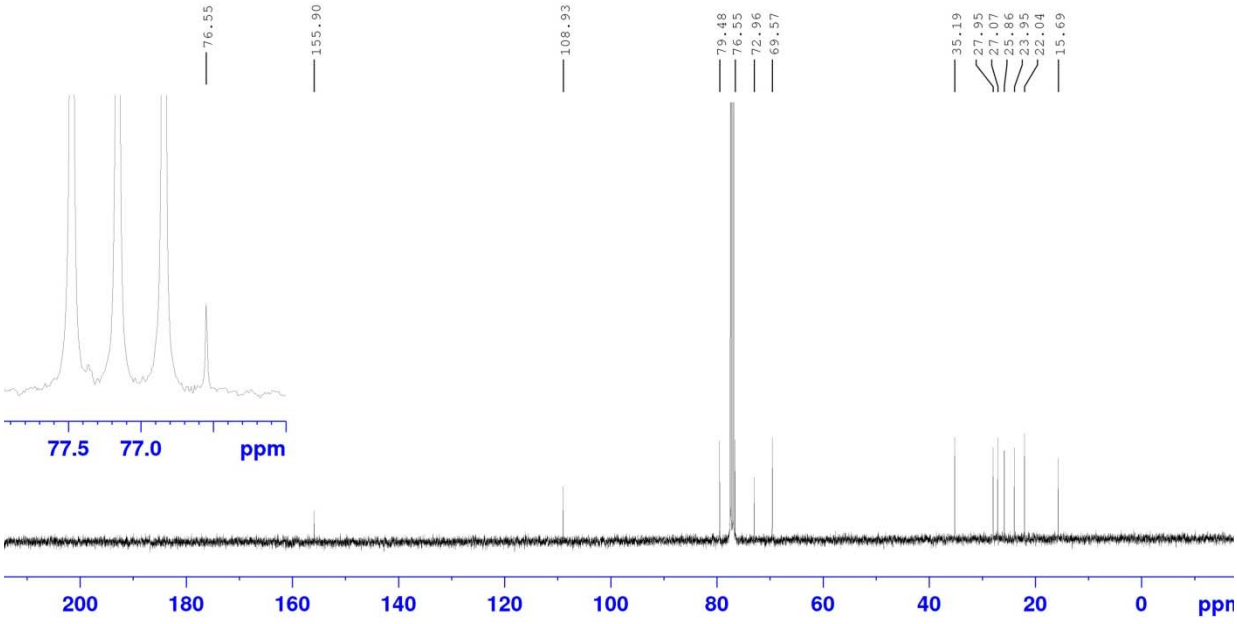


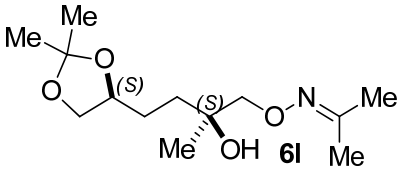
6l

^{1}H NMR



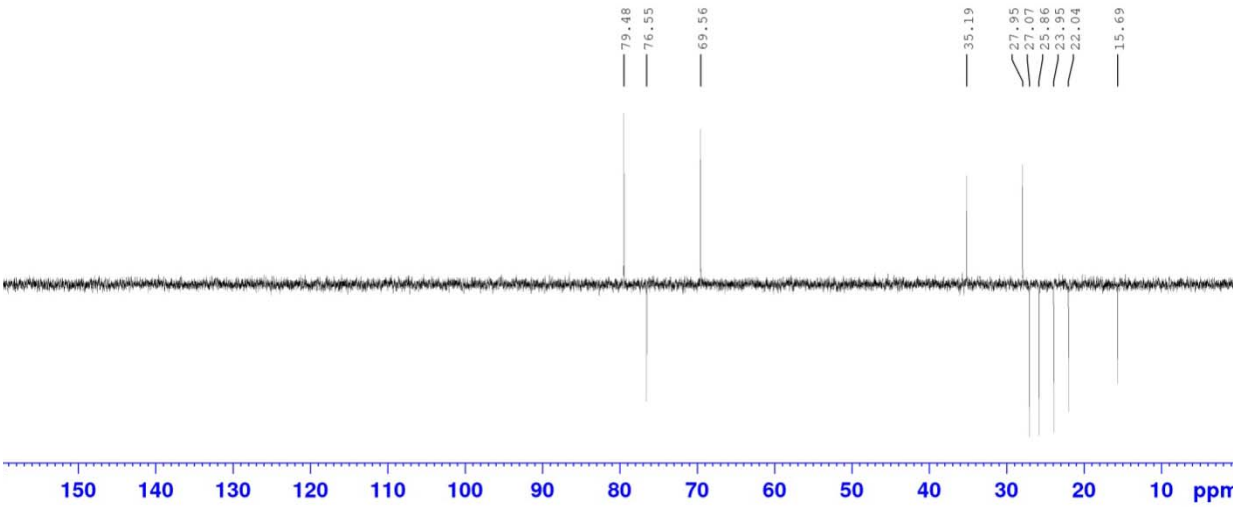
^{13}C NMR



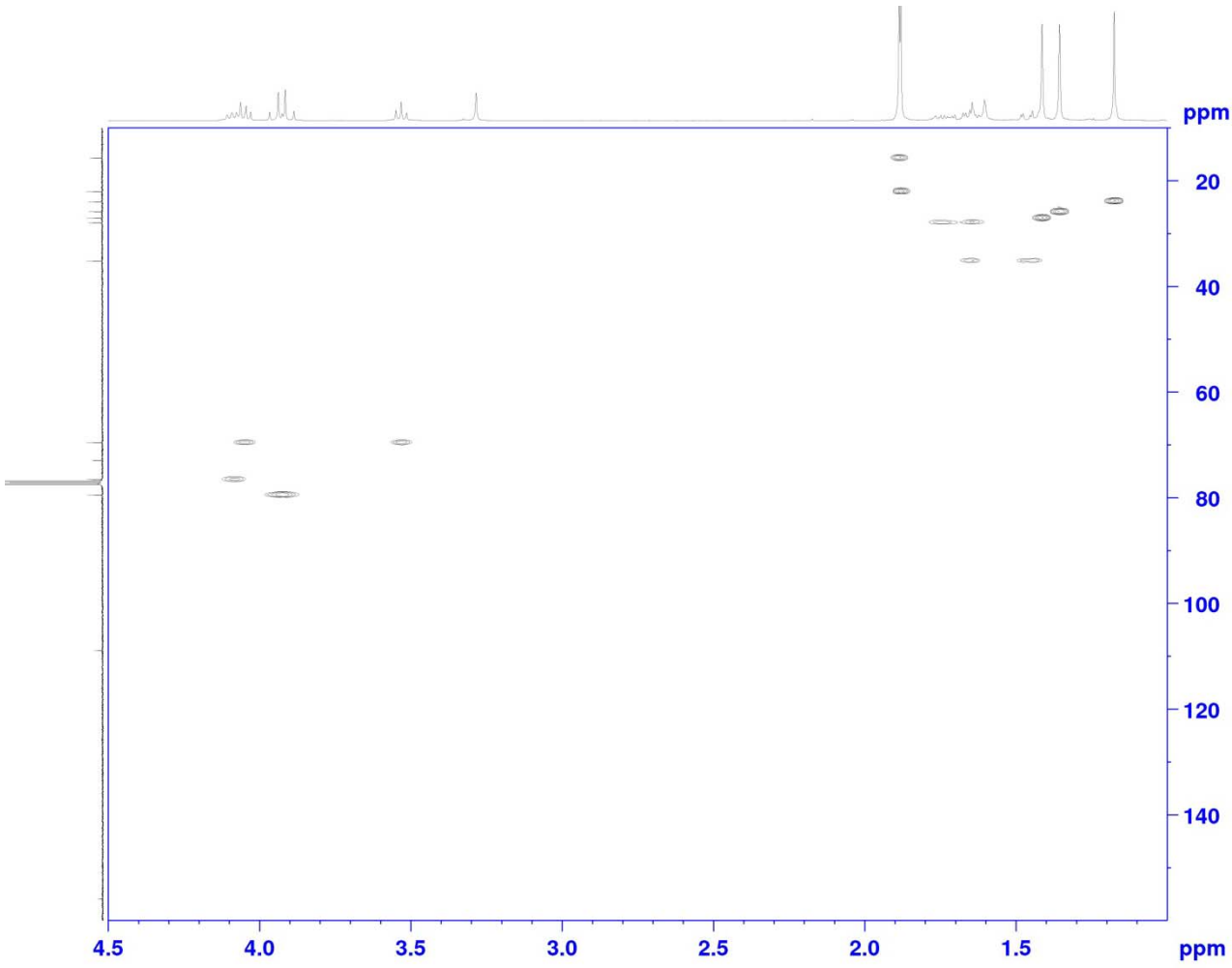


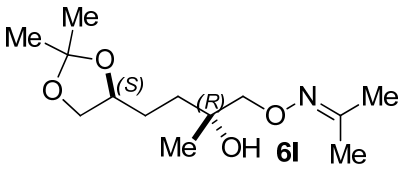
6l

^{13}C DEPT 135 NMR



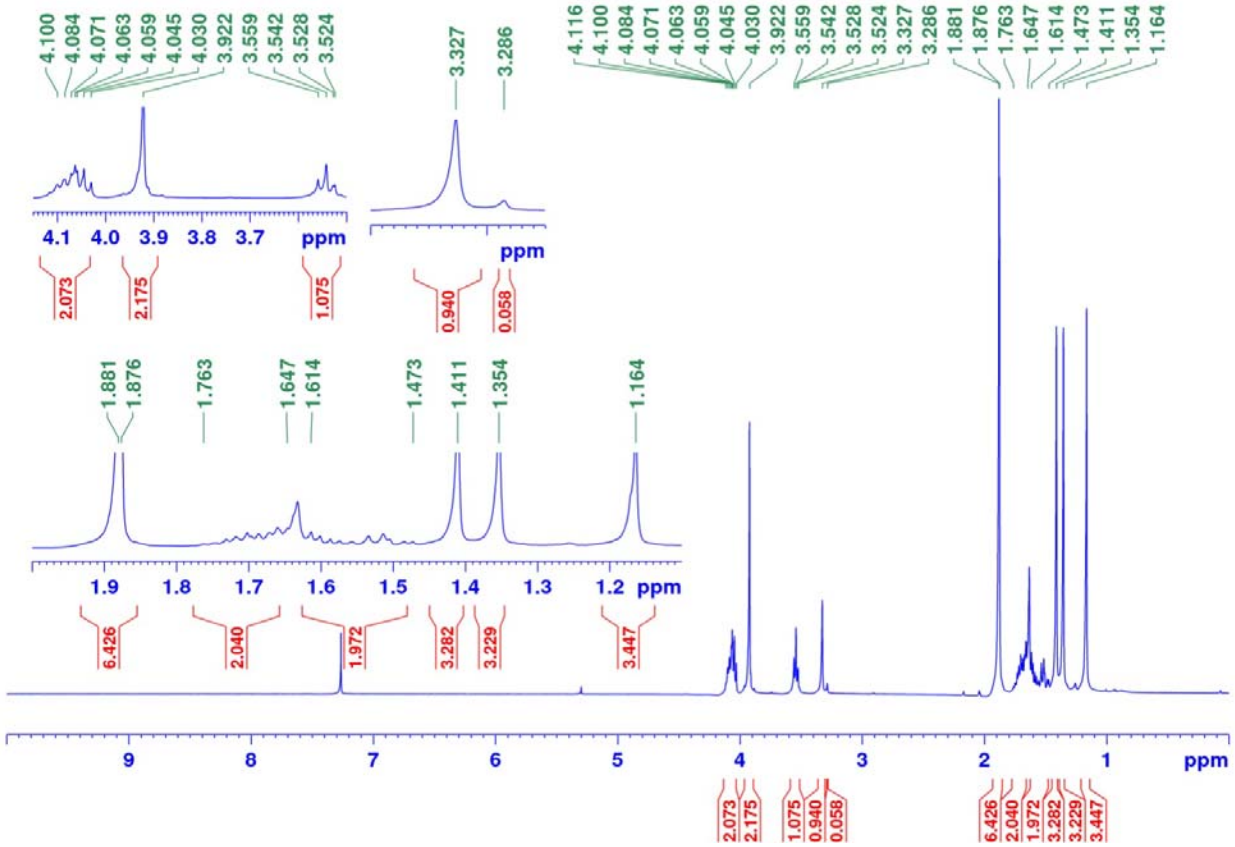
^{1}H-^{13}C HSQC



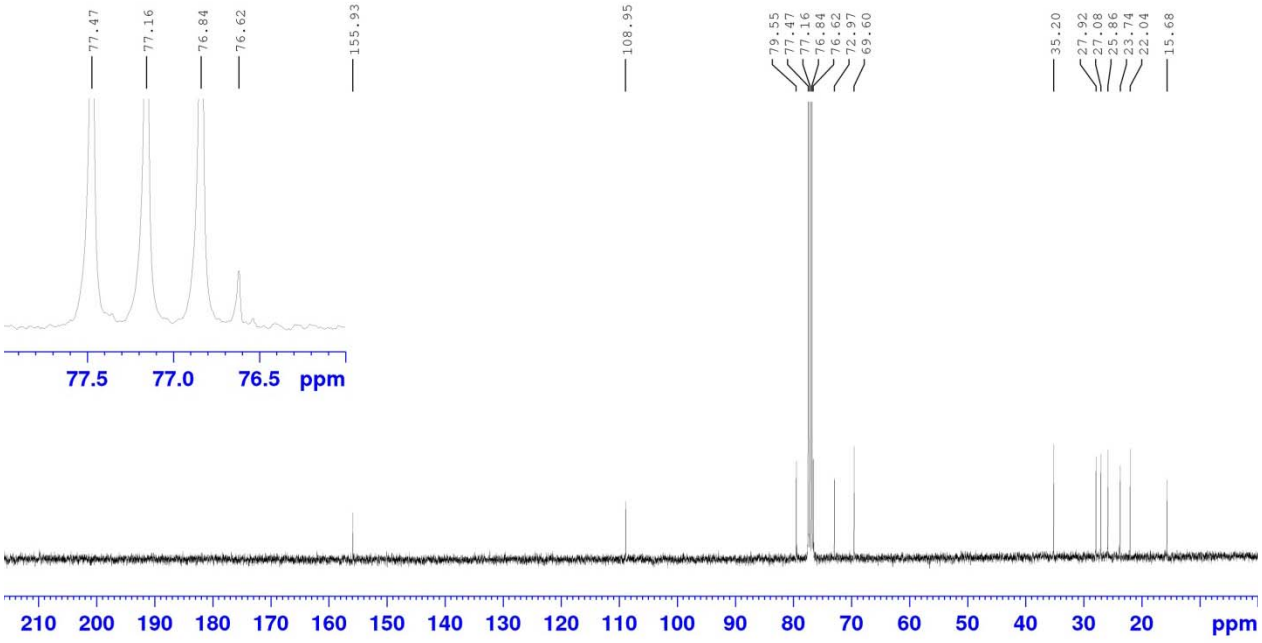


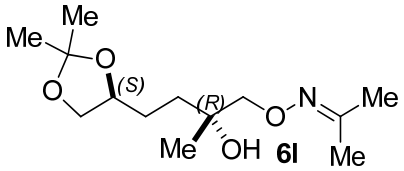
6l

^{1}H NMR



^{13}C NMR





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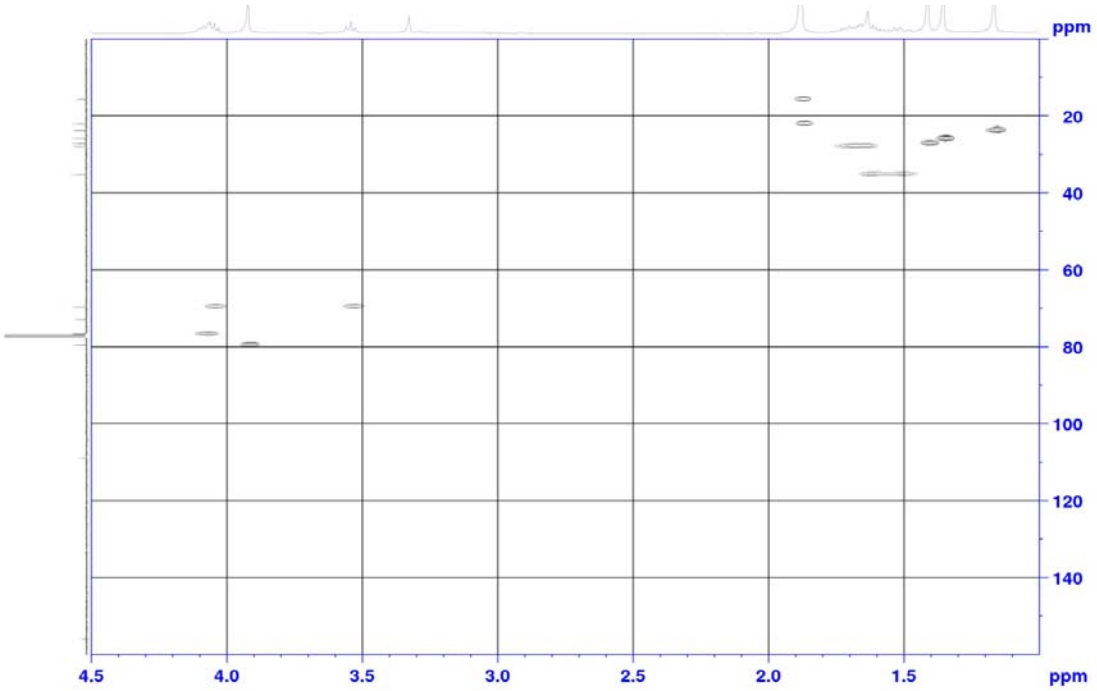
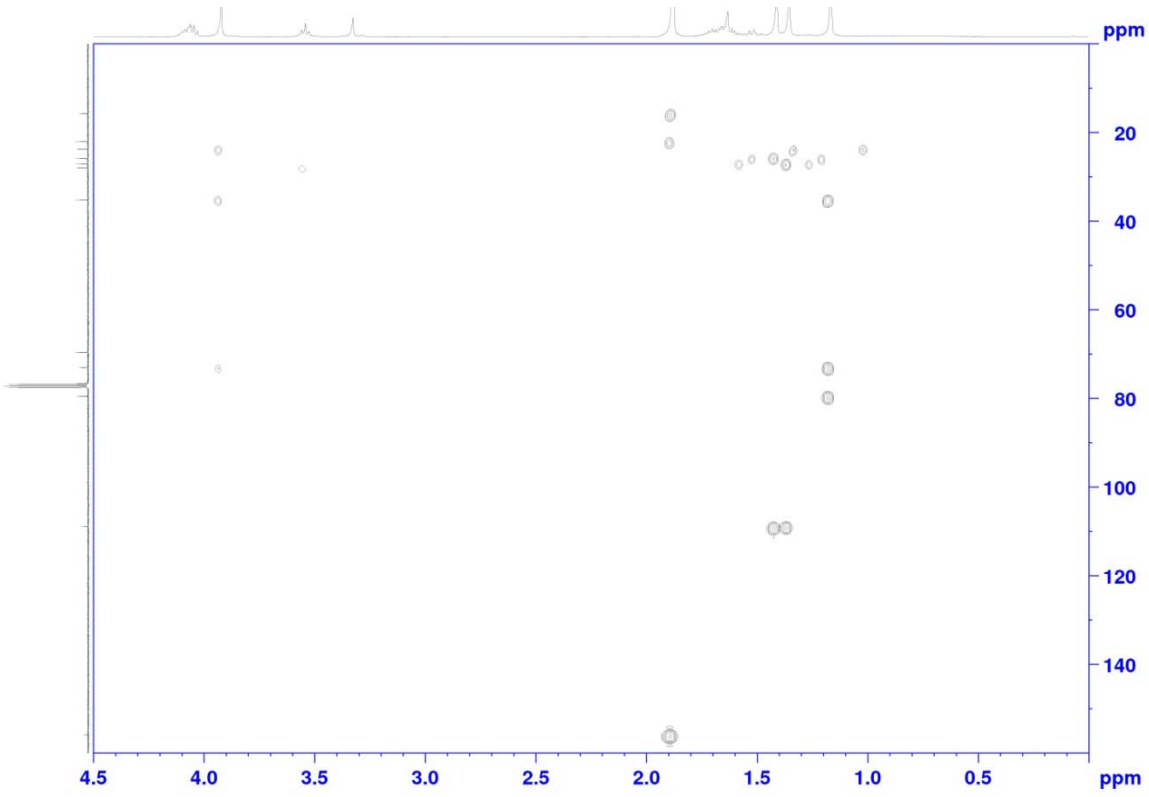
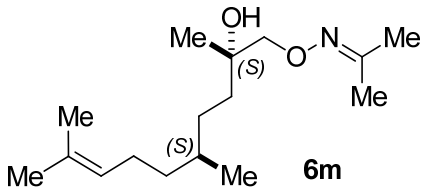
^{1}H-^{13}C HSQC



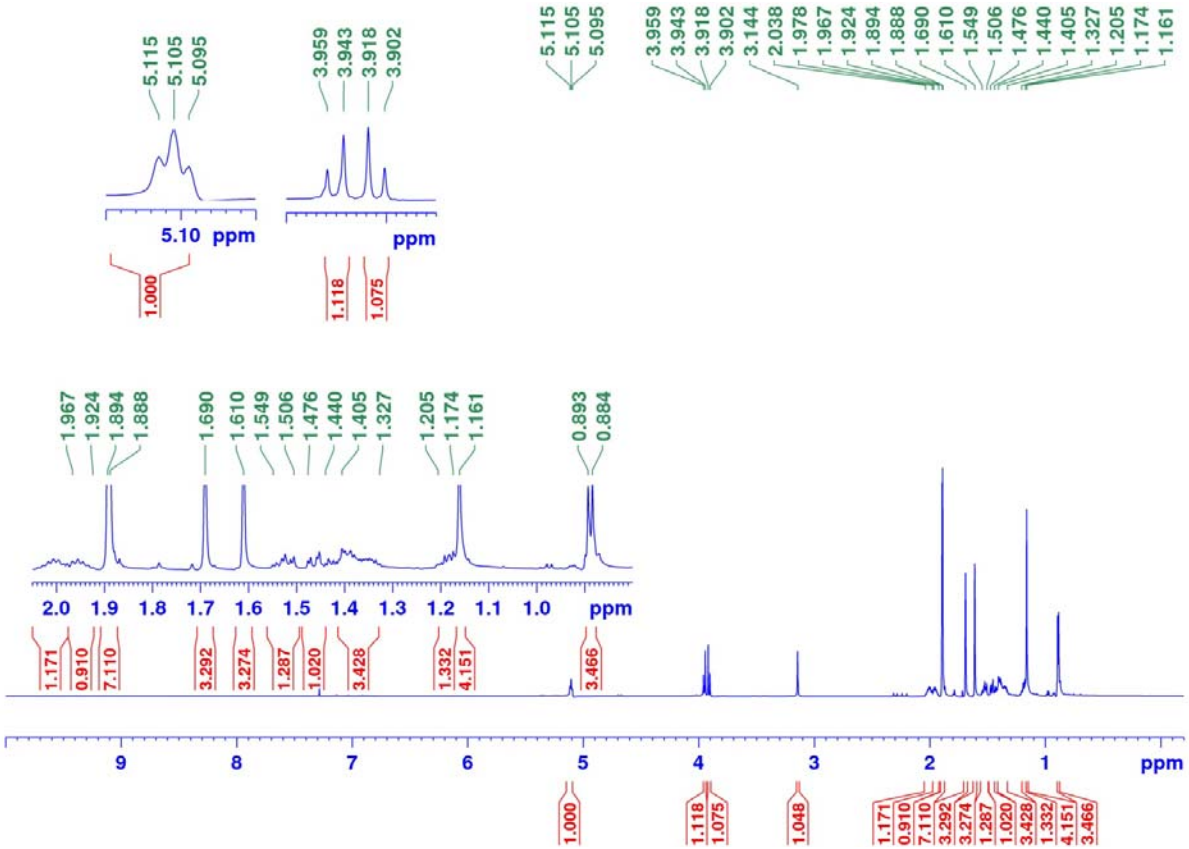
^{1}H-^{13}C HMBC NMR



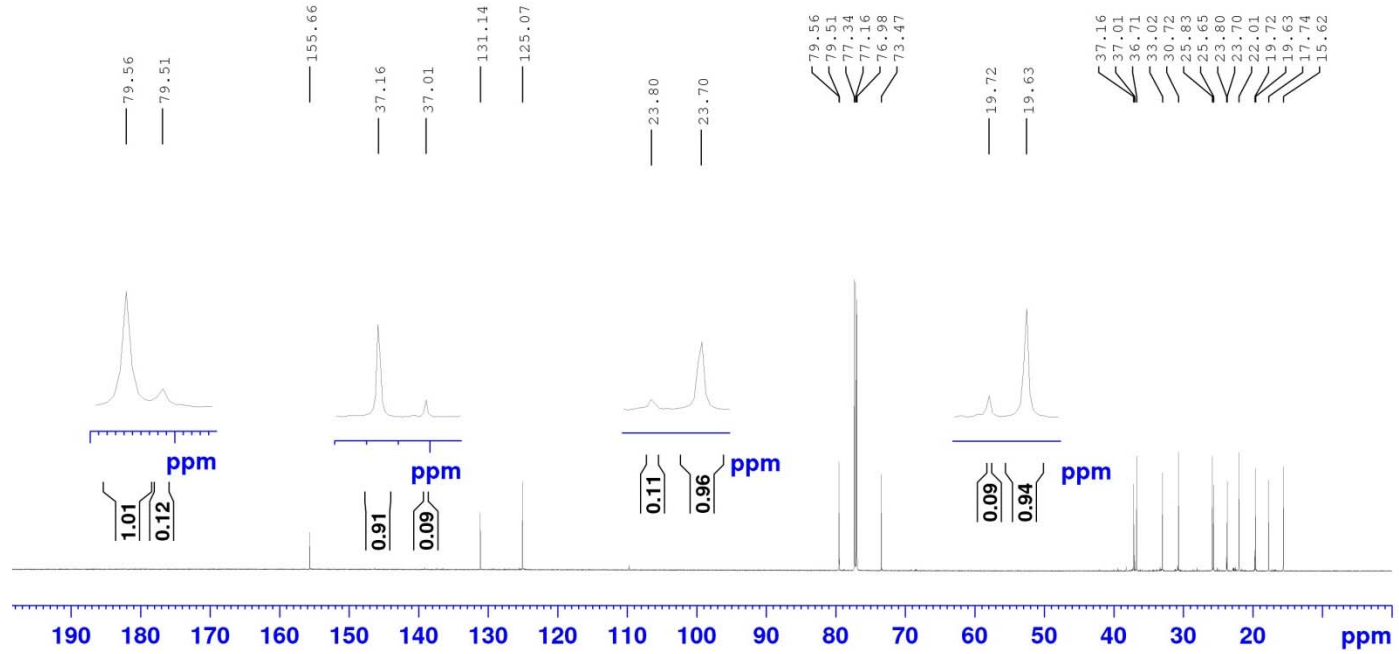
^{1}H NMR

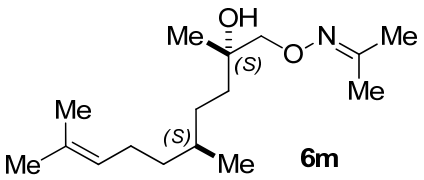


6m



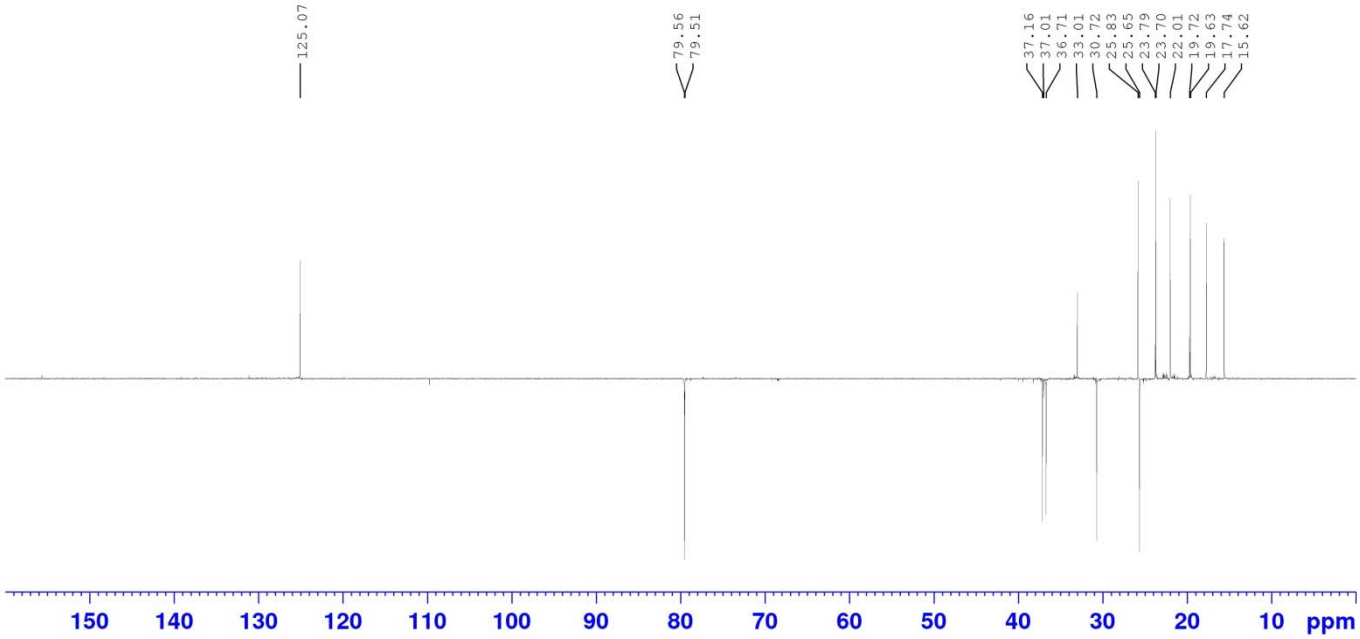
^{13}C NMR



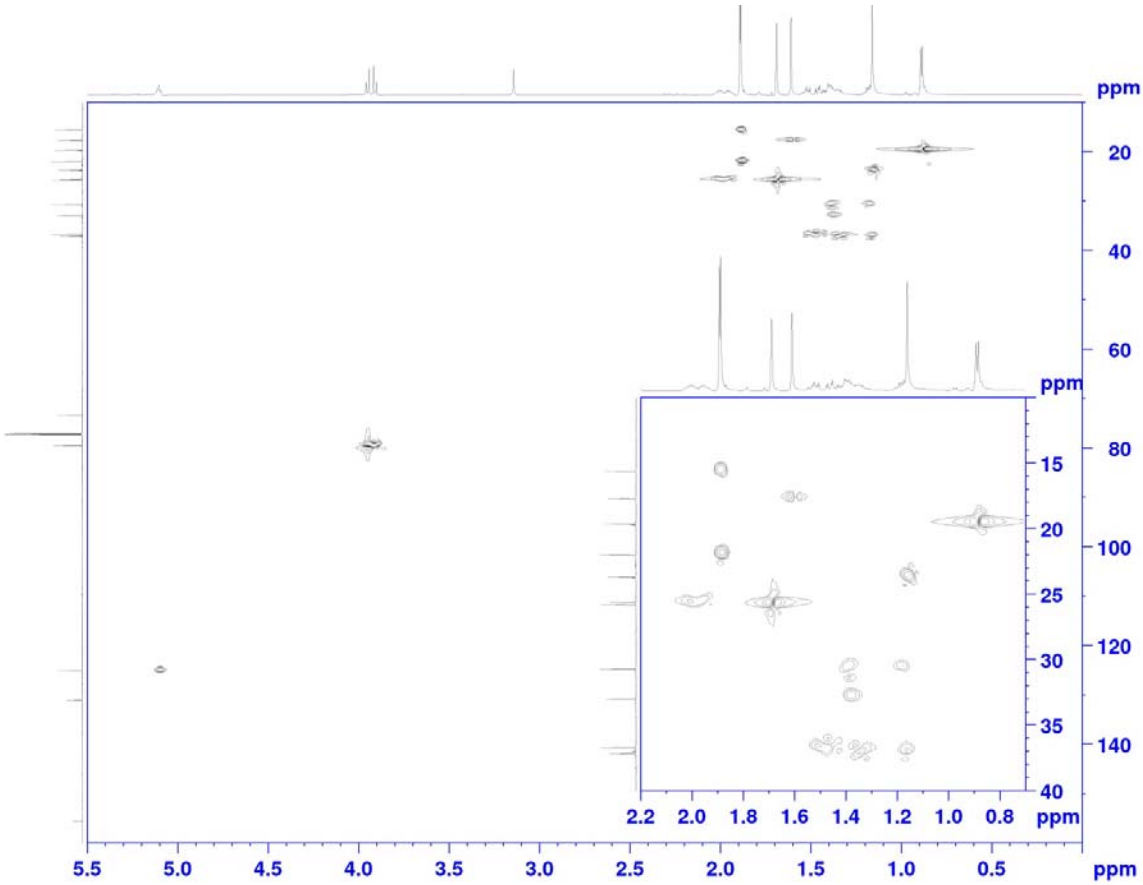


6m

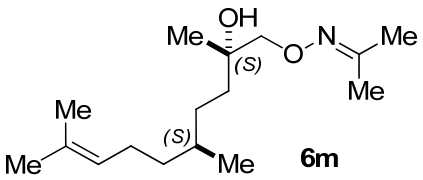
^{13}C DEPT 135 NMR



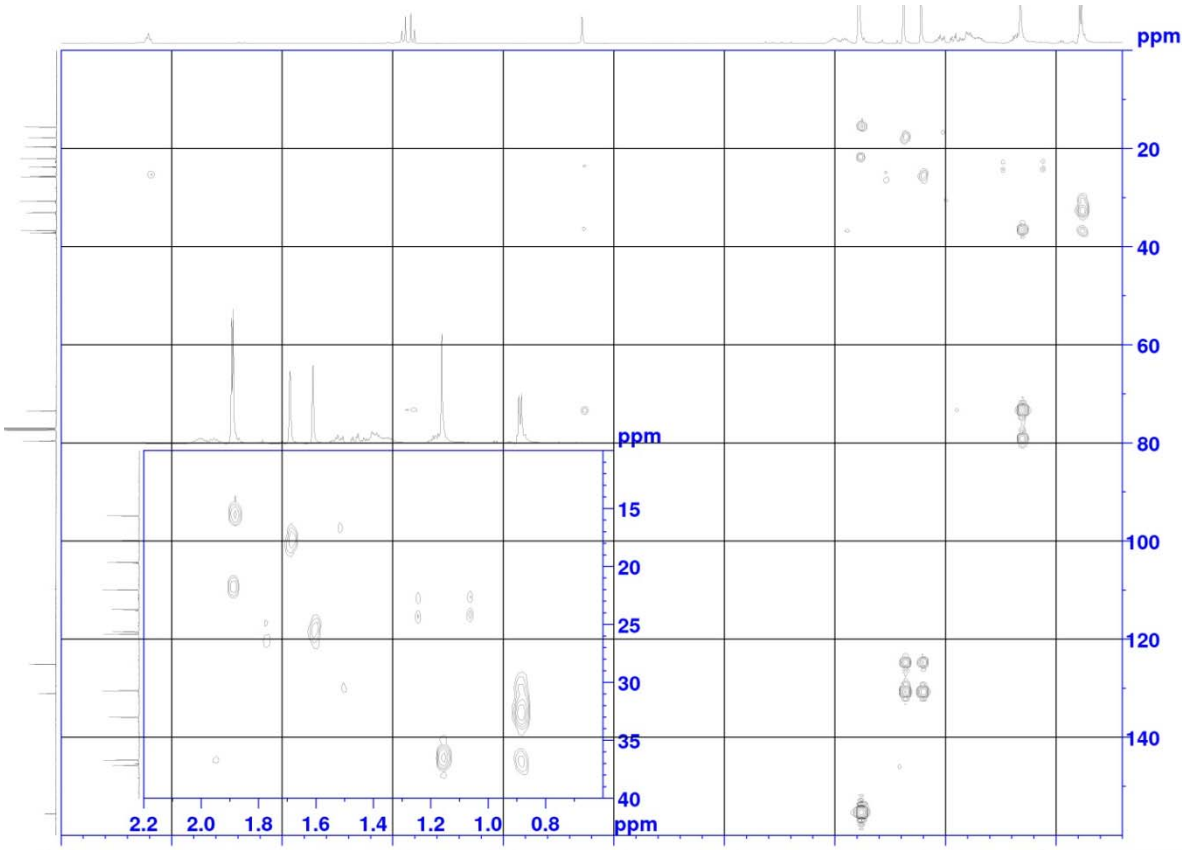
^{1}H- ^{13}C HSQC NMR

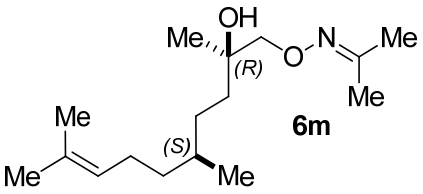


^{1}H- ^{13}C HMBC NMR



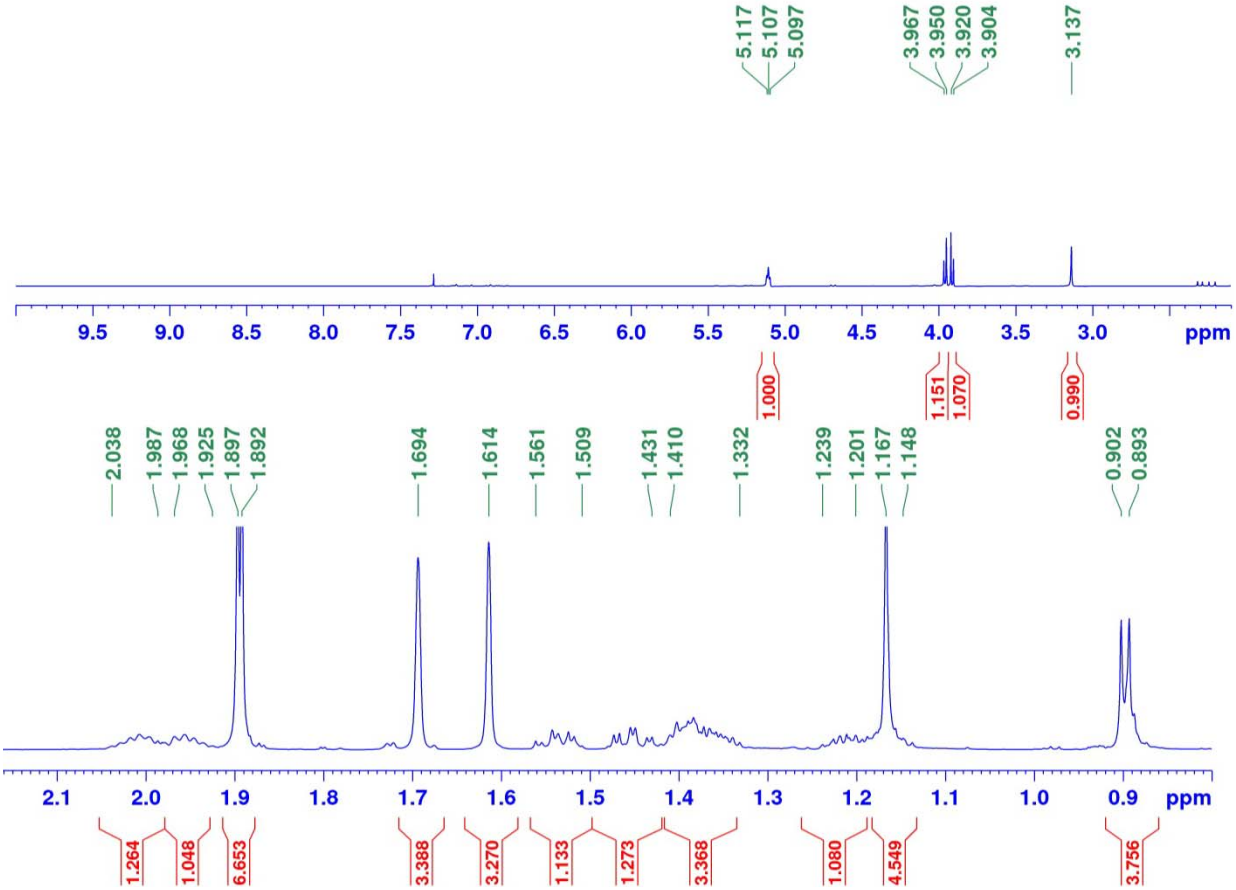
6m



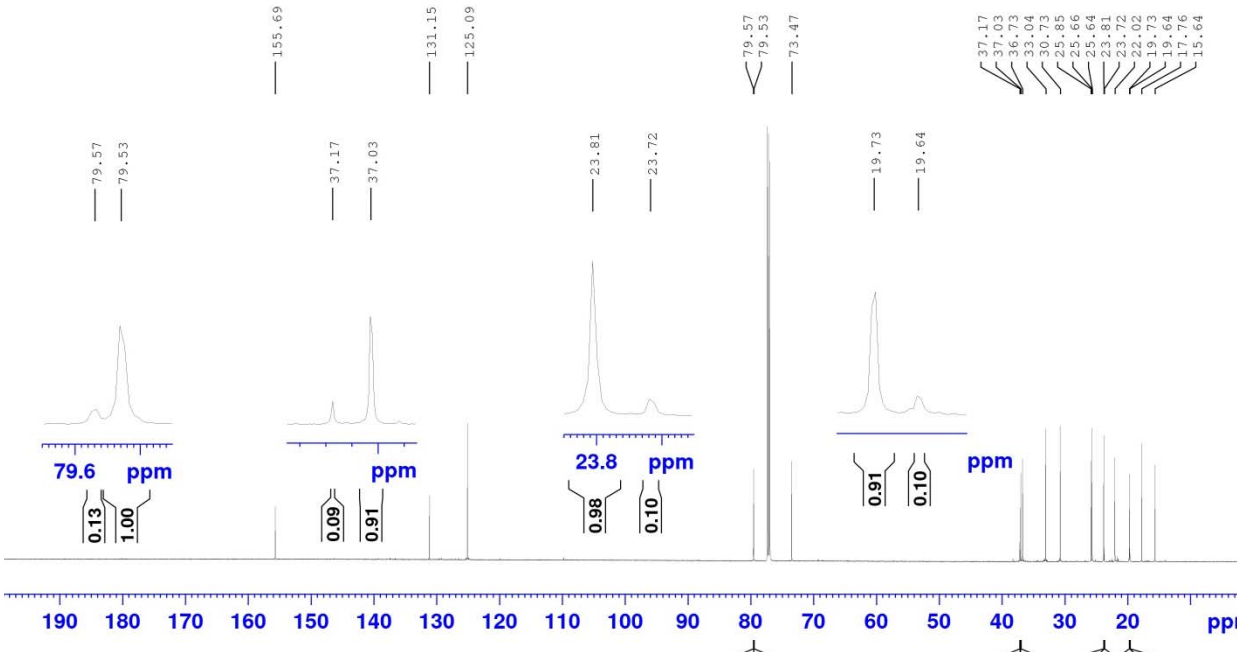


6m

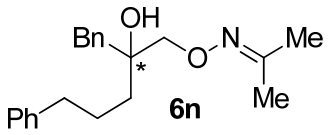
^{1}H NMR

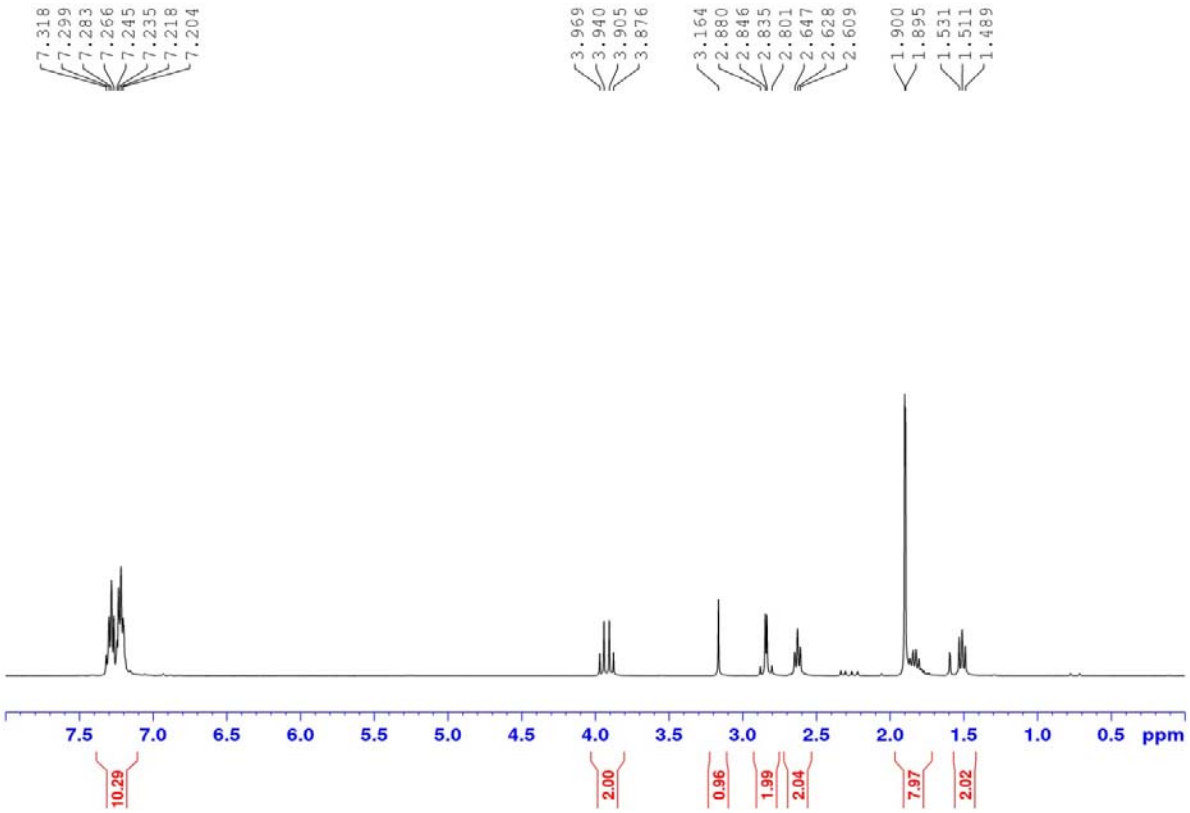


^{13}C NMR

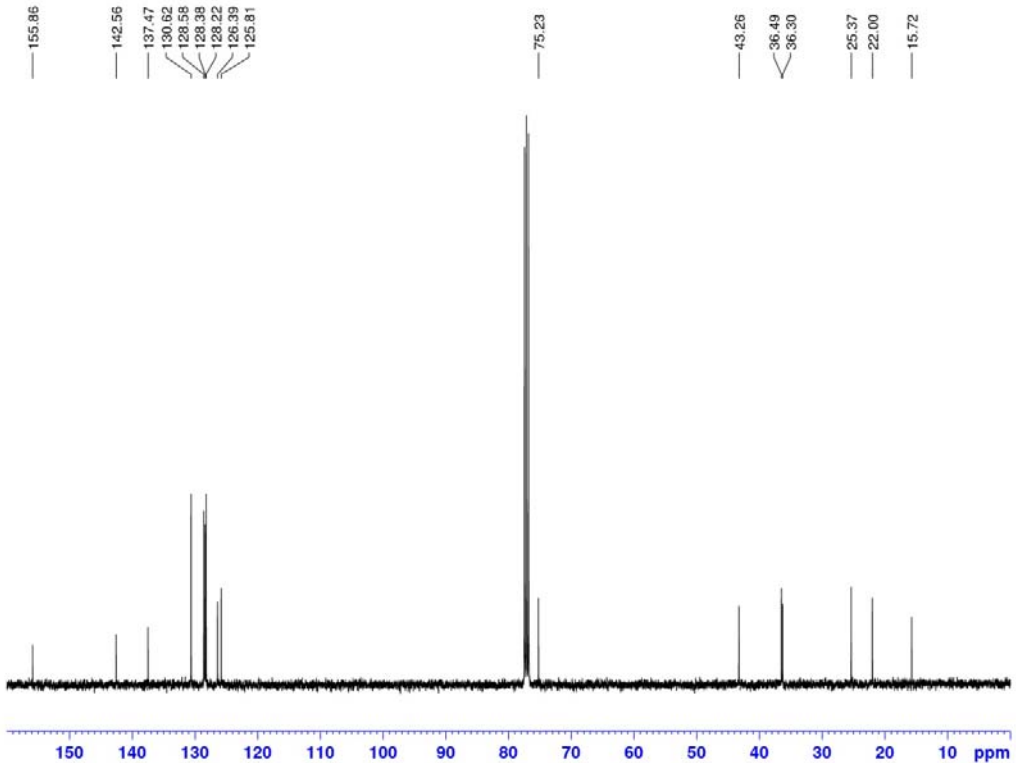


^{1}H- NMR

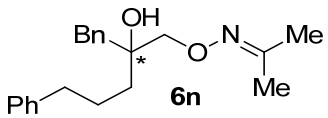


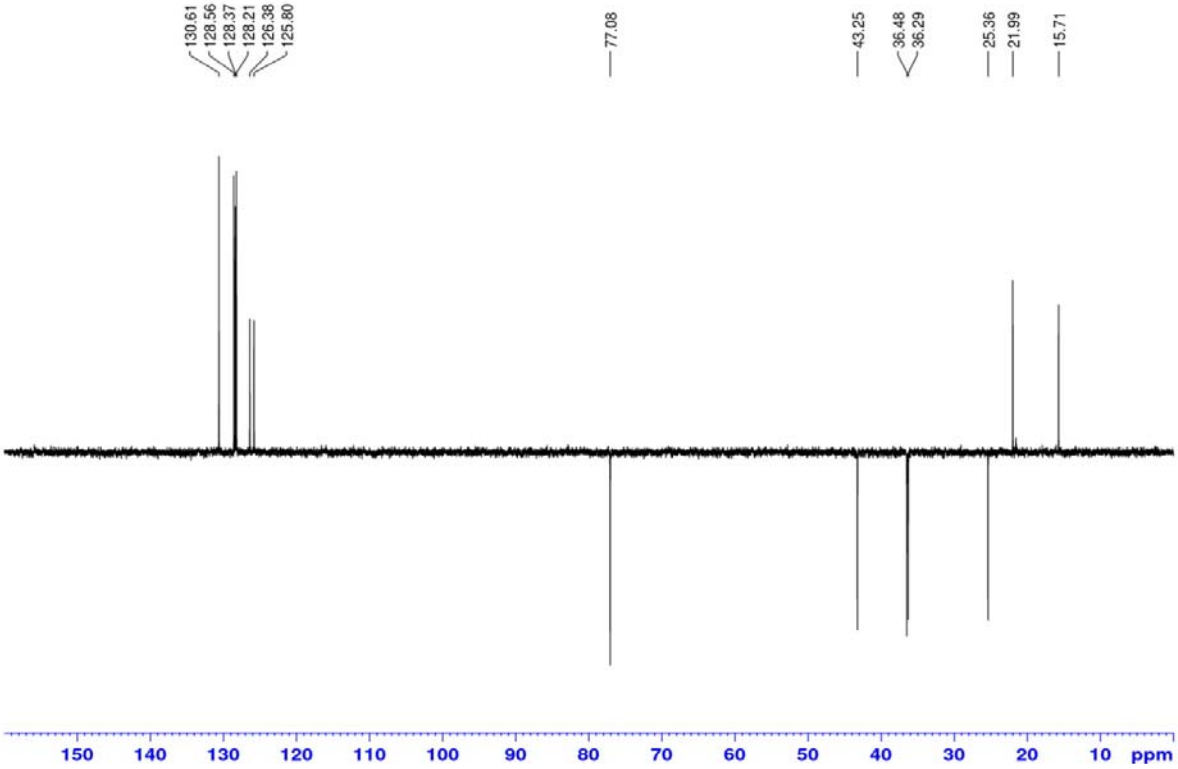


^{13}C- NMR

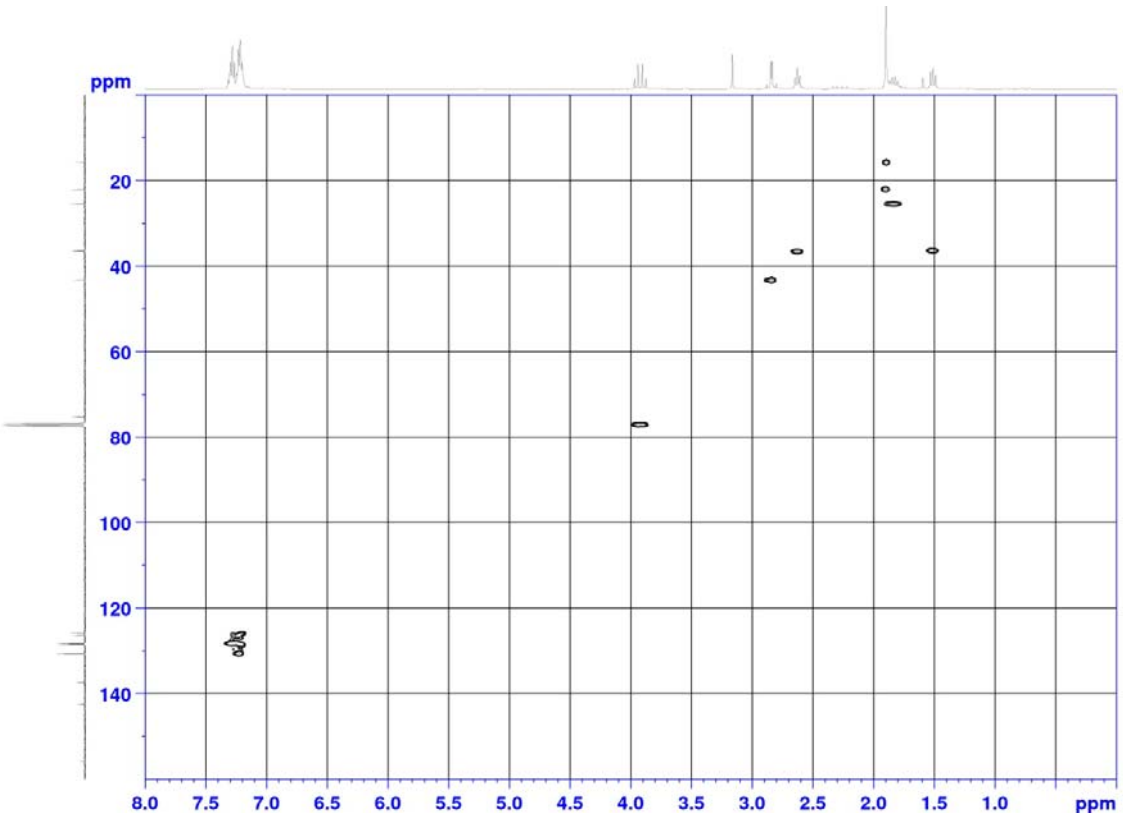


^{13}C DEPT 135 NMR

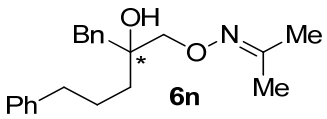




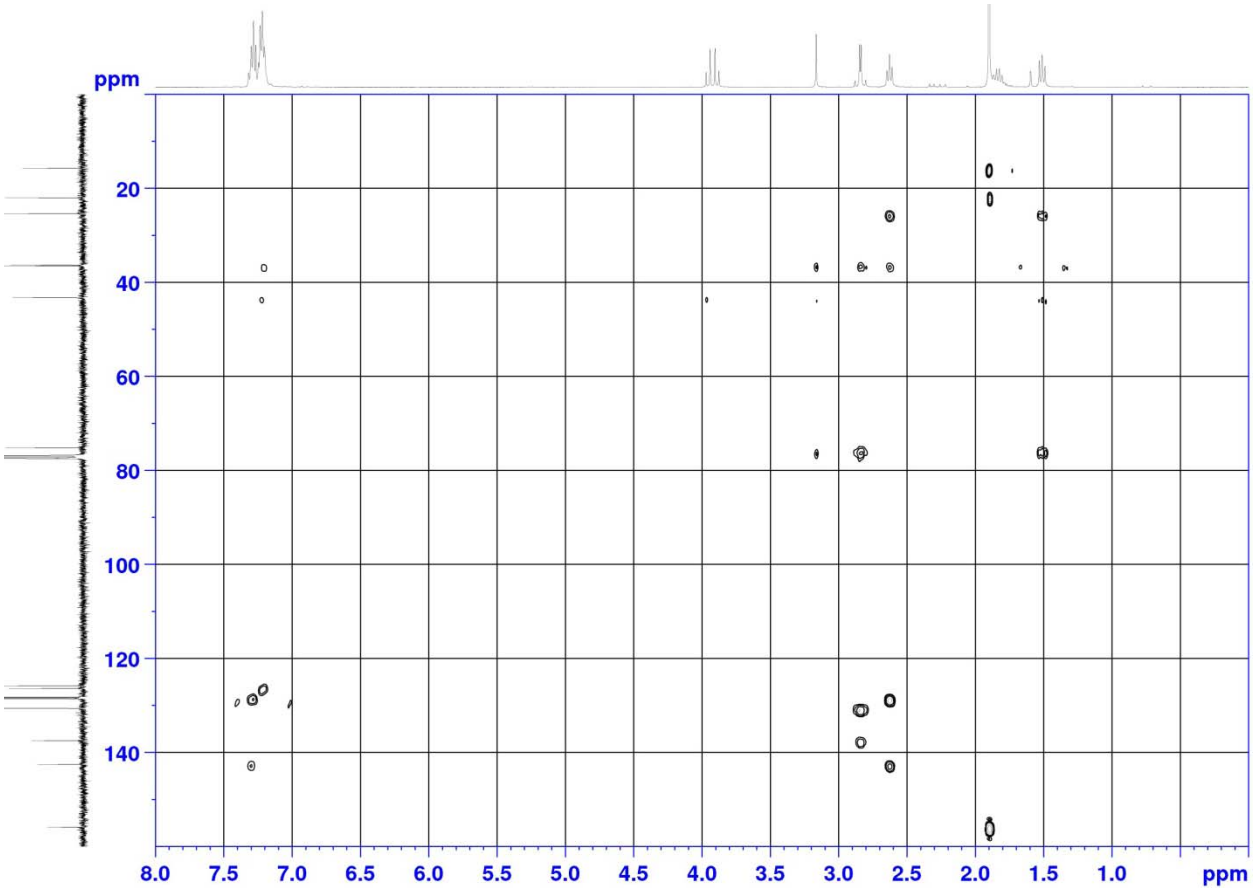
^{1}H- ^{13}C HSQC NMR



^{1}H- ^{13}C HMBC NMR

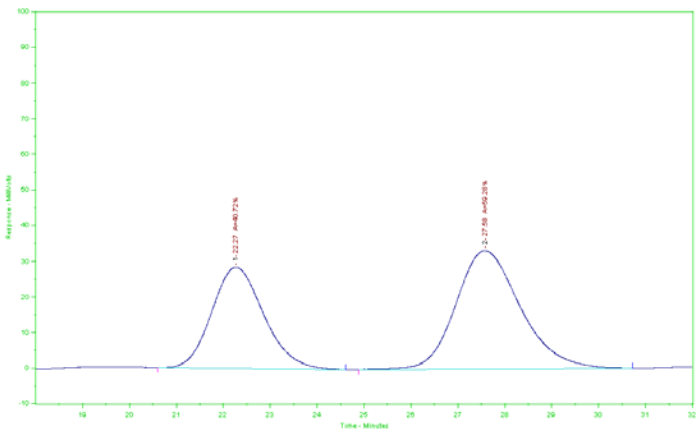


6n

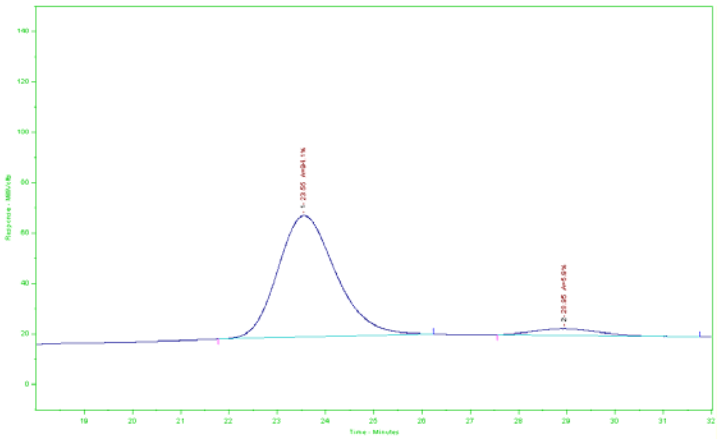


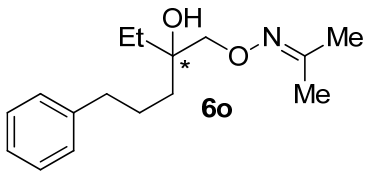
HPLC traces (Chiralpak-OD, 97:3 hexanes:isopropanol @ 1.0 mL/min)

a) racemic mixture



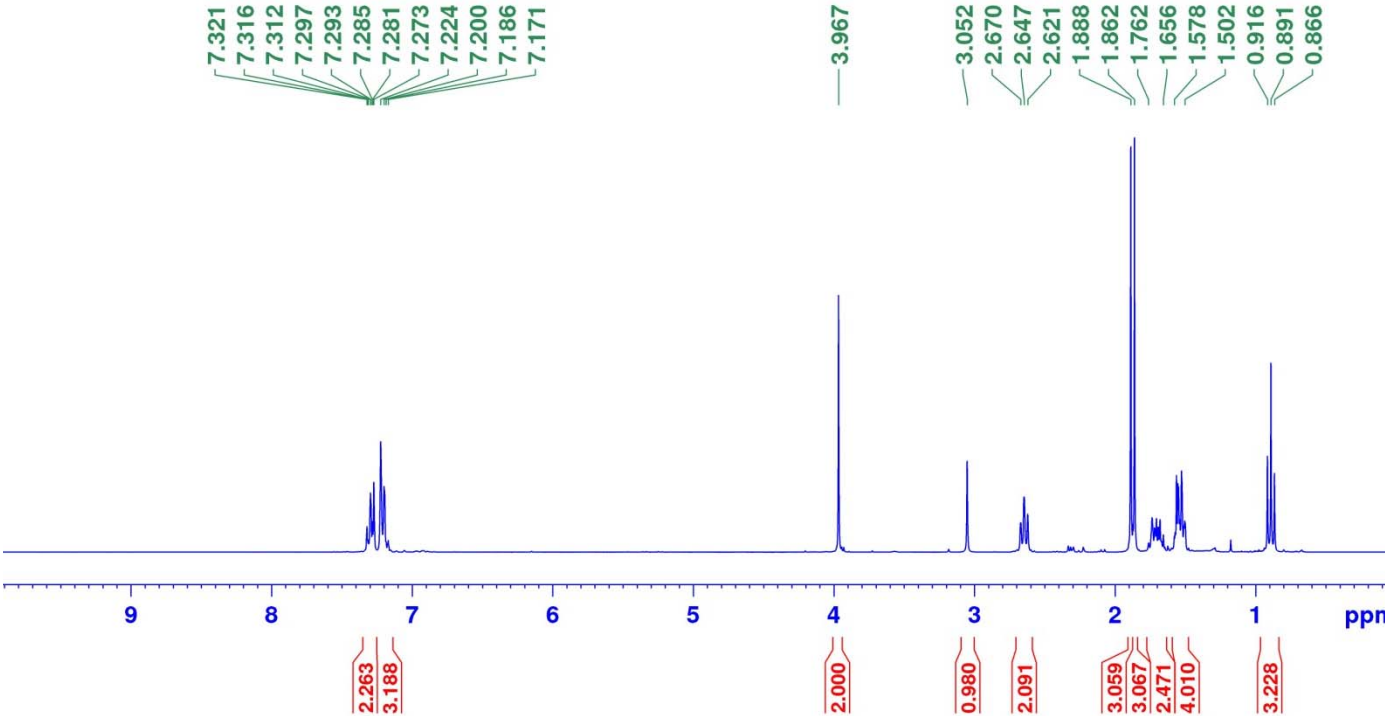
b) *S*:*R* = 94:6 after CAHB of **10n** with (*R*,*R*)-**L**



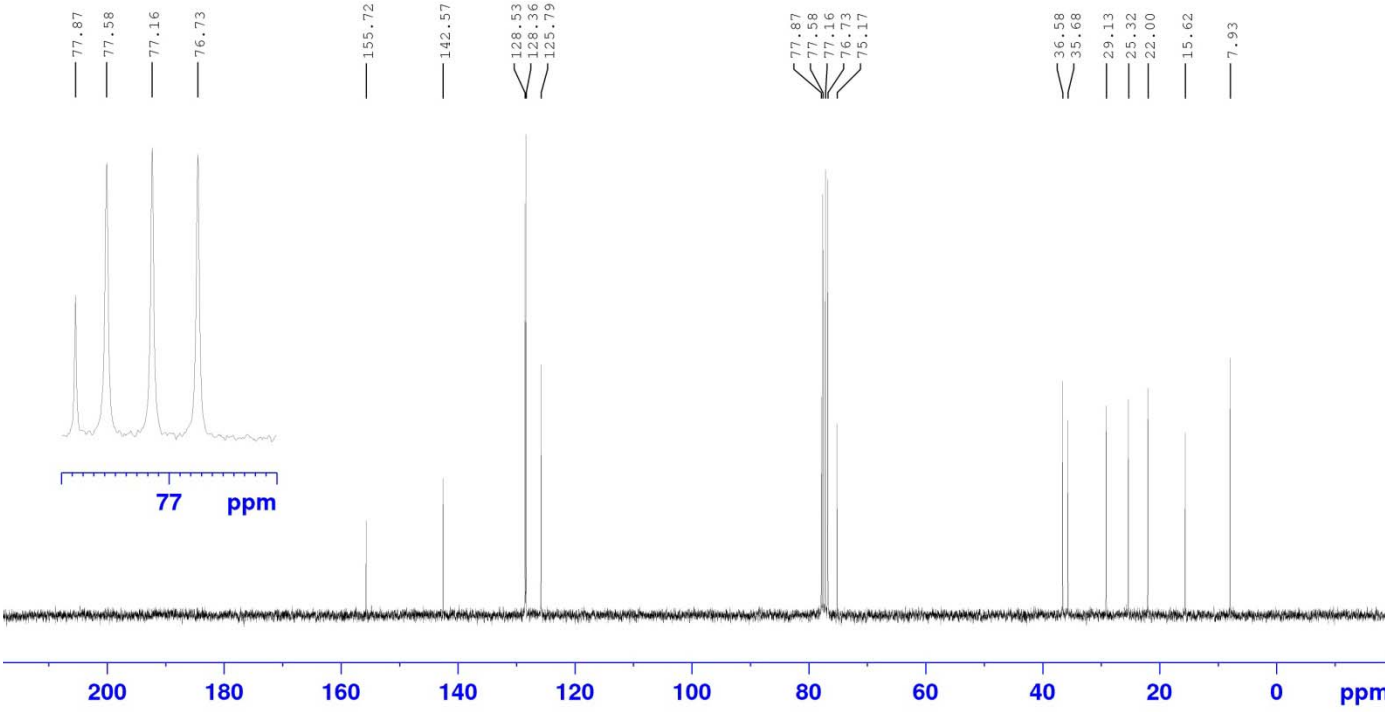


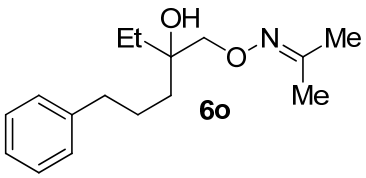
6o

^{1}H NMR



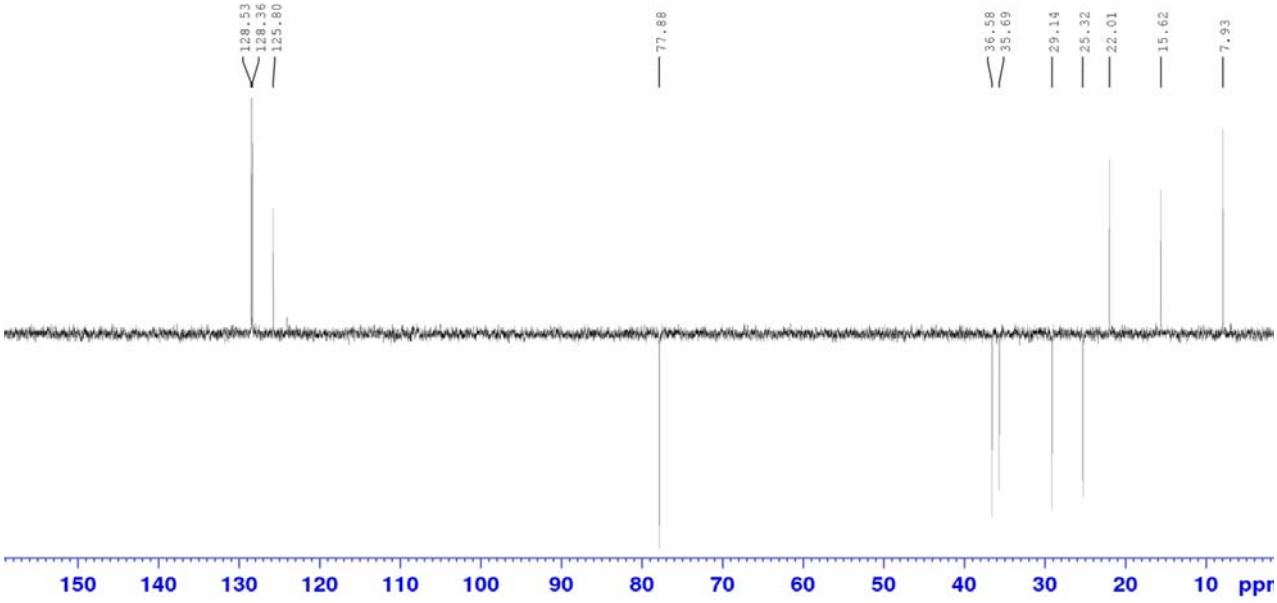
^{13}C NMR



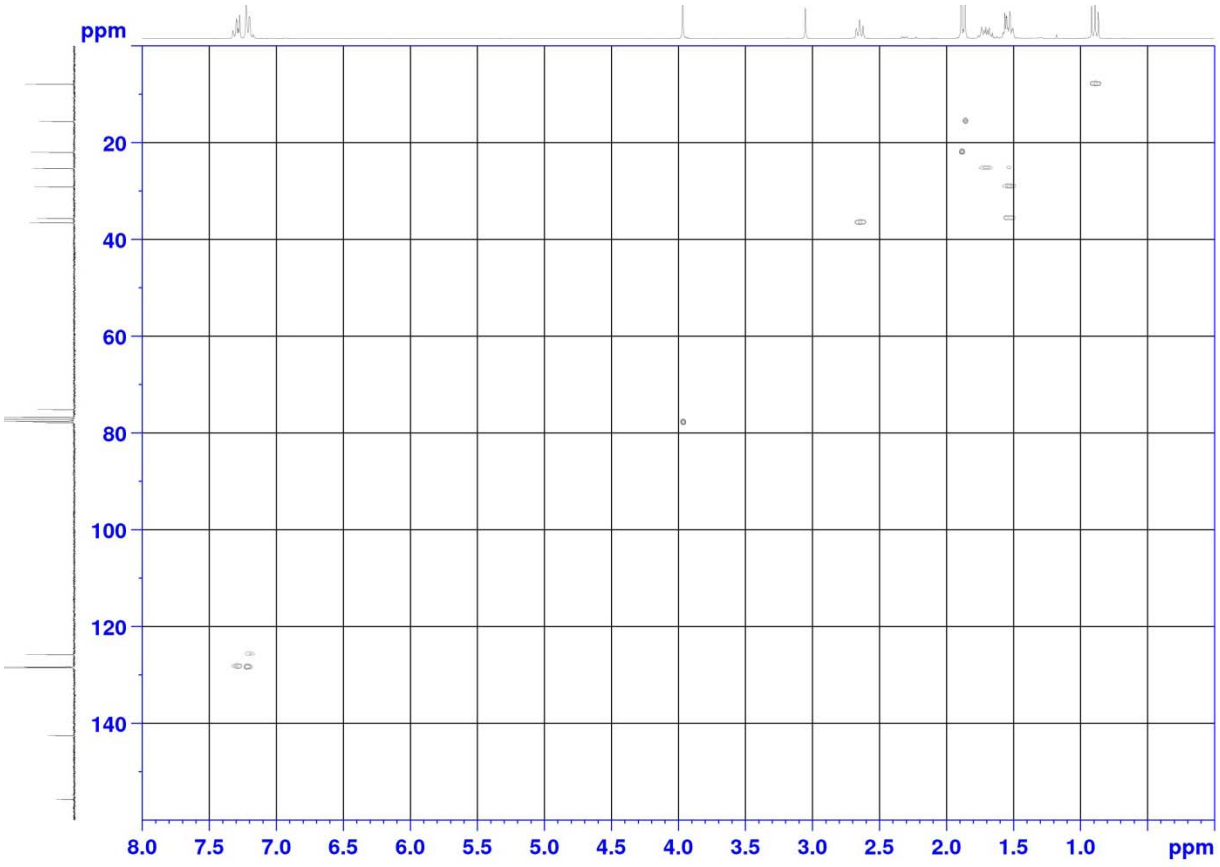


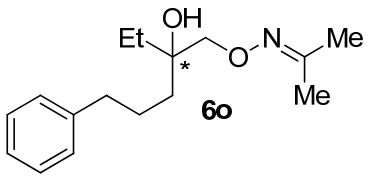
6o

^{13}C DEPT 135 NMR



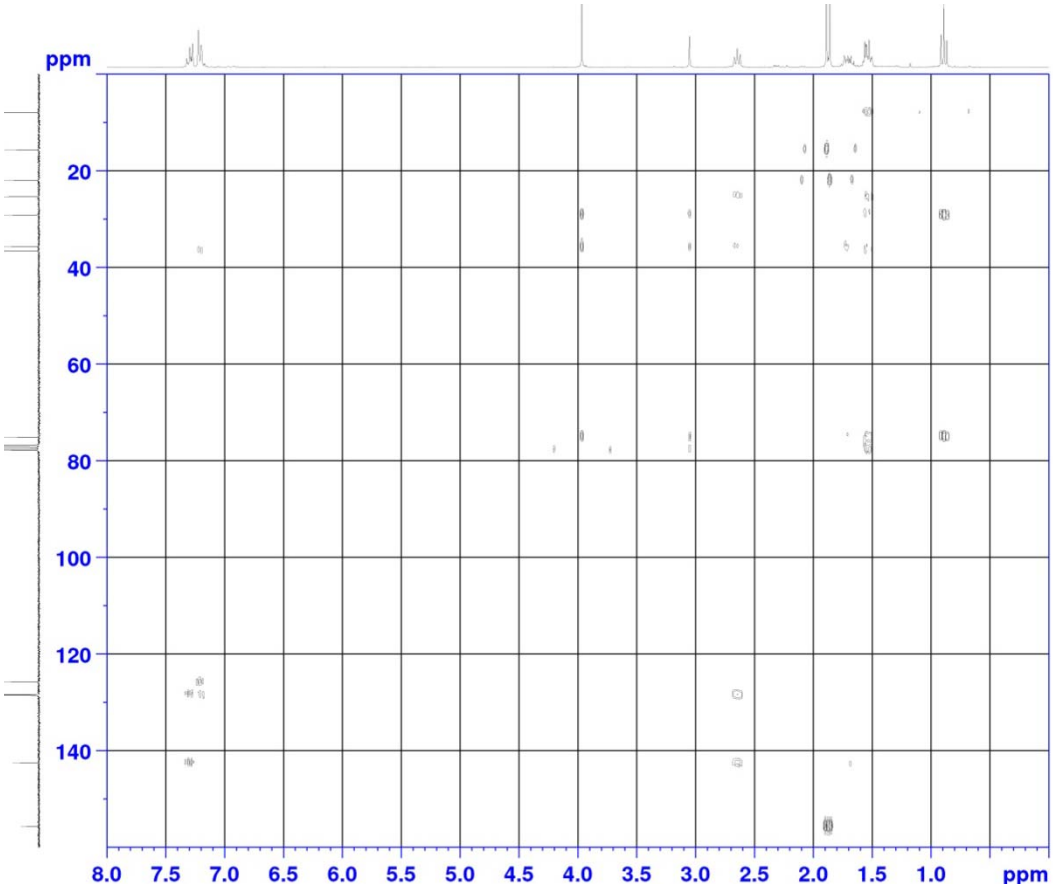
^{1}H- ^{13}C HSQC NMR





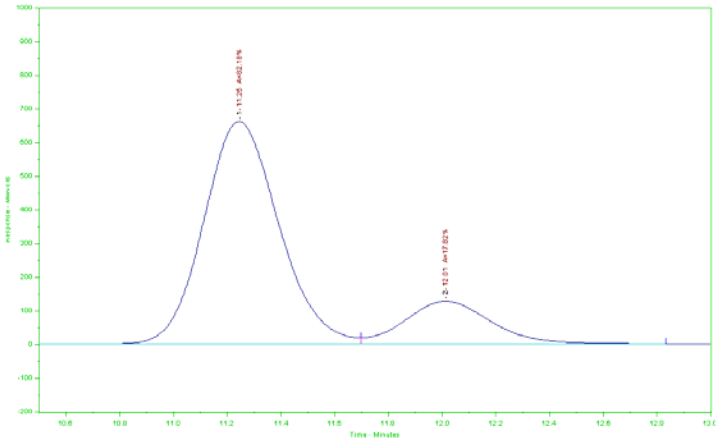
6o

^{1}H- ^{13}C HMBC NMR

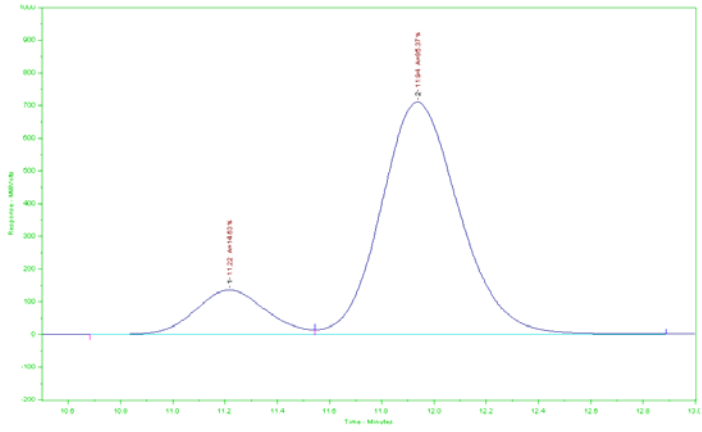


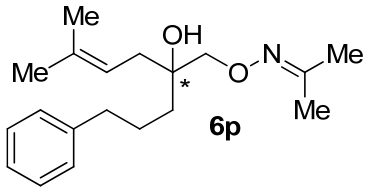
HPLC traces (Chiralpak-AD, 90:10 hexanes:isopropanol @ 1.0 mL/min)

a) *S:R* = 82:18 after CAHB of **10o** with (*R,R*)-**L**

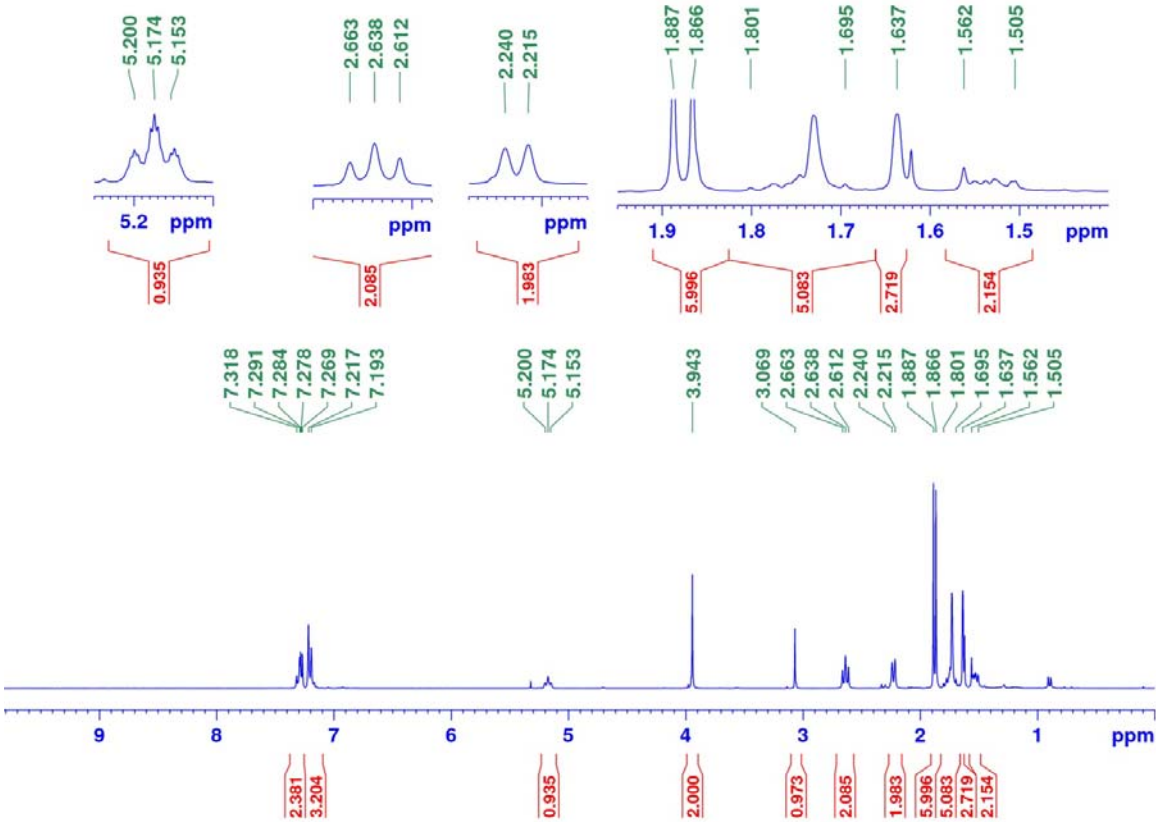


b) *S:R* = 15:85 after CAHB of **10o** with (*S,S*)-**L**

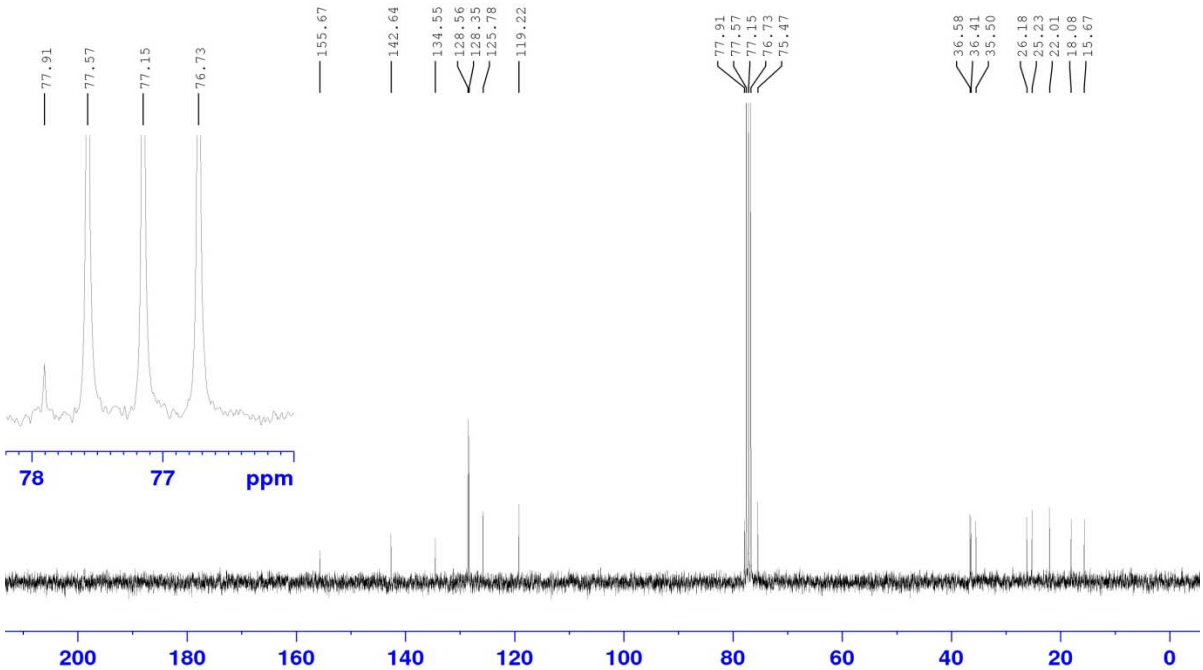


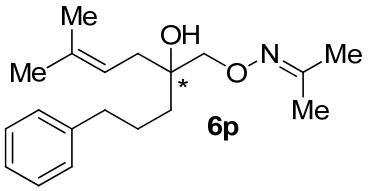


^{1}H NMR



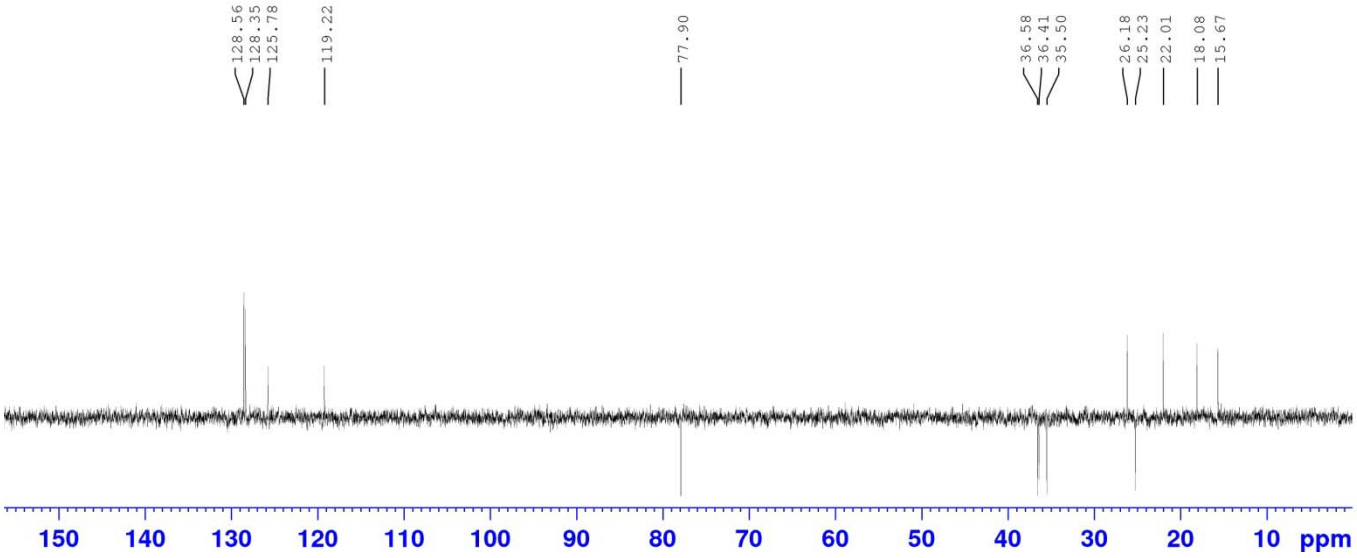
^{13}C NMR



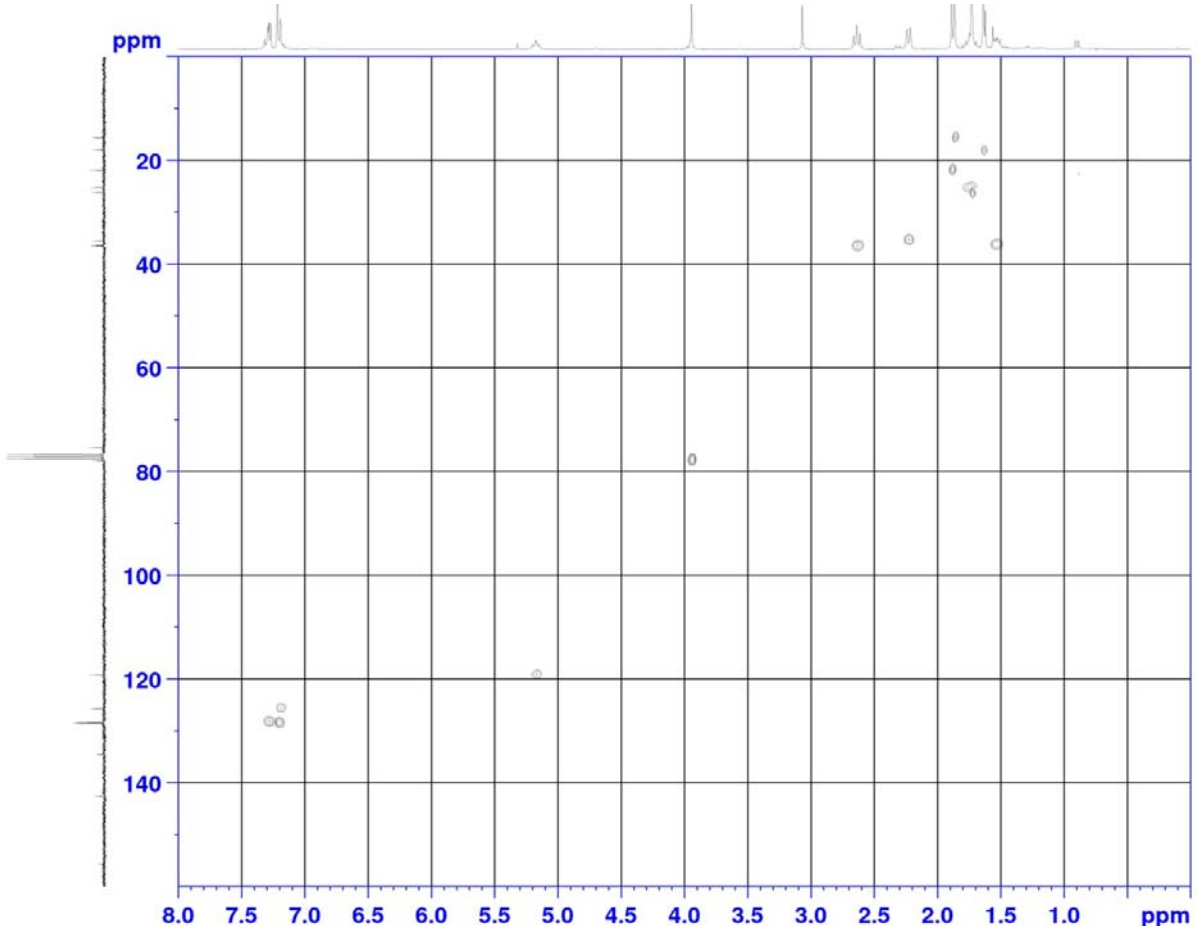


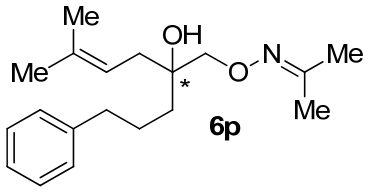
6p

^{13}C DEPT NMR



^{1}H-^{13}C HSQC NMR

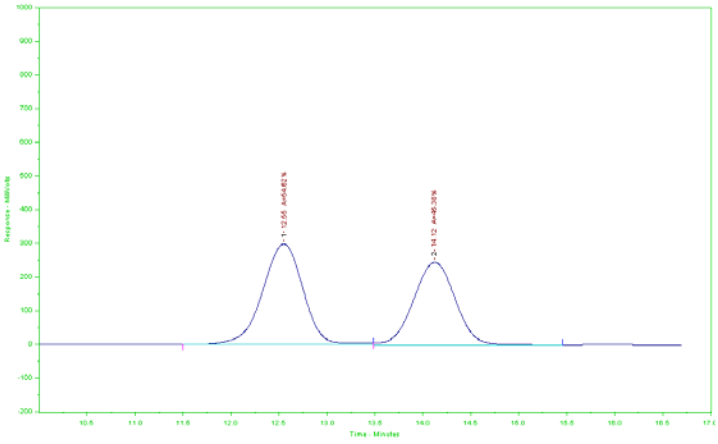




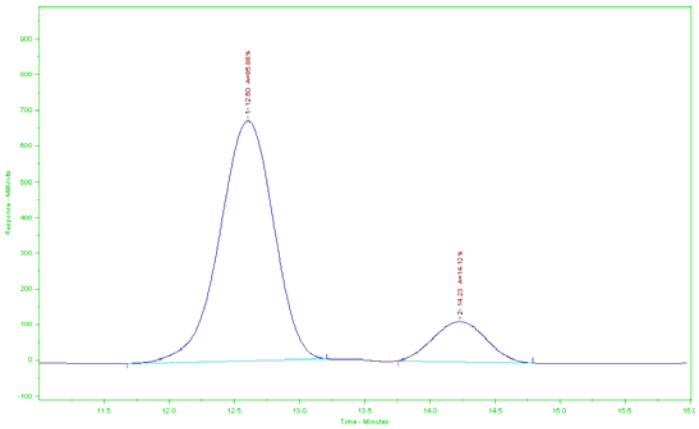
6p

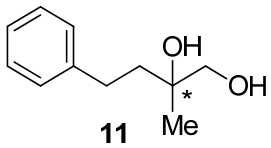
HPLC traces (Chiralpak-IB, 97:3 hexanes:isopropanol @ 1.0 mL/min)

a) racemic mixture



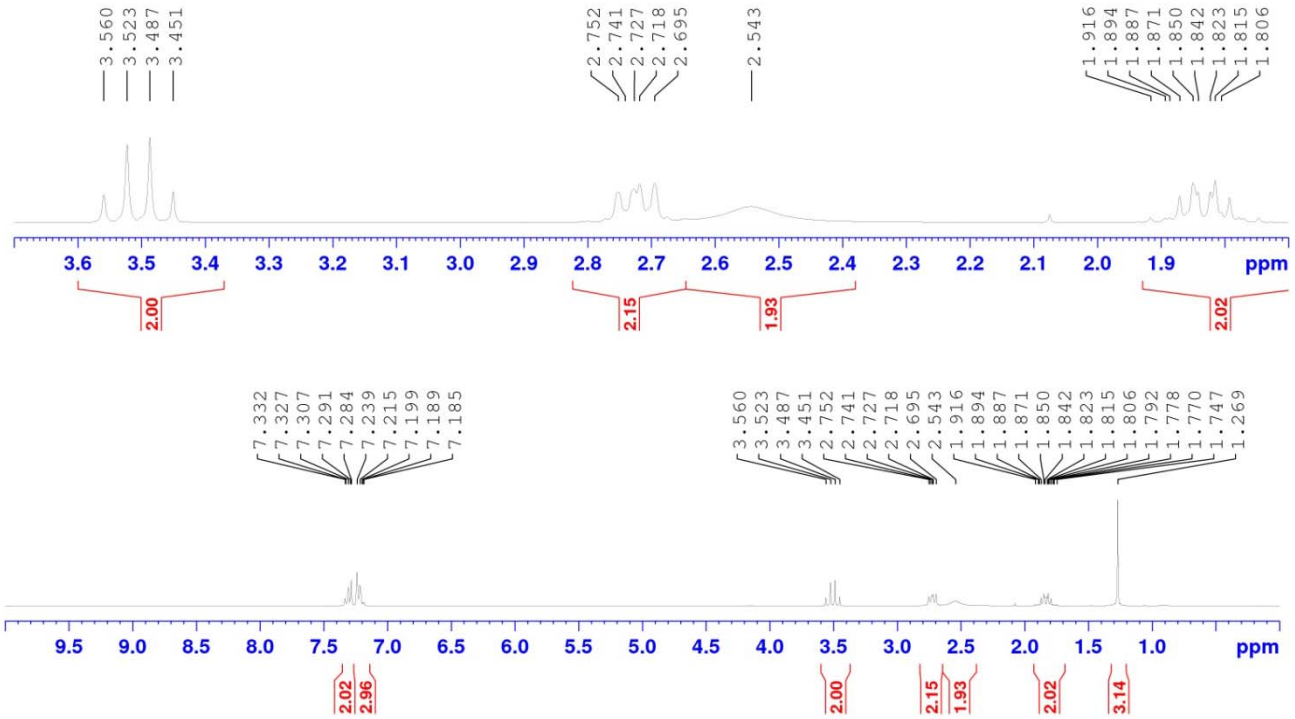
b) *S:R*=86:14 after CAHB of **10p** with (*R*,*R*)-**L**



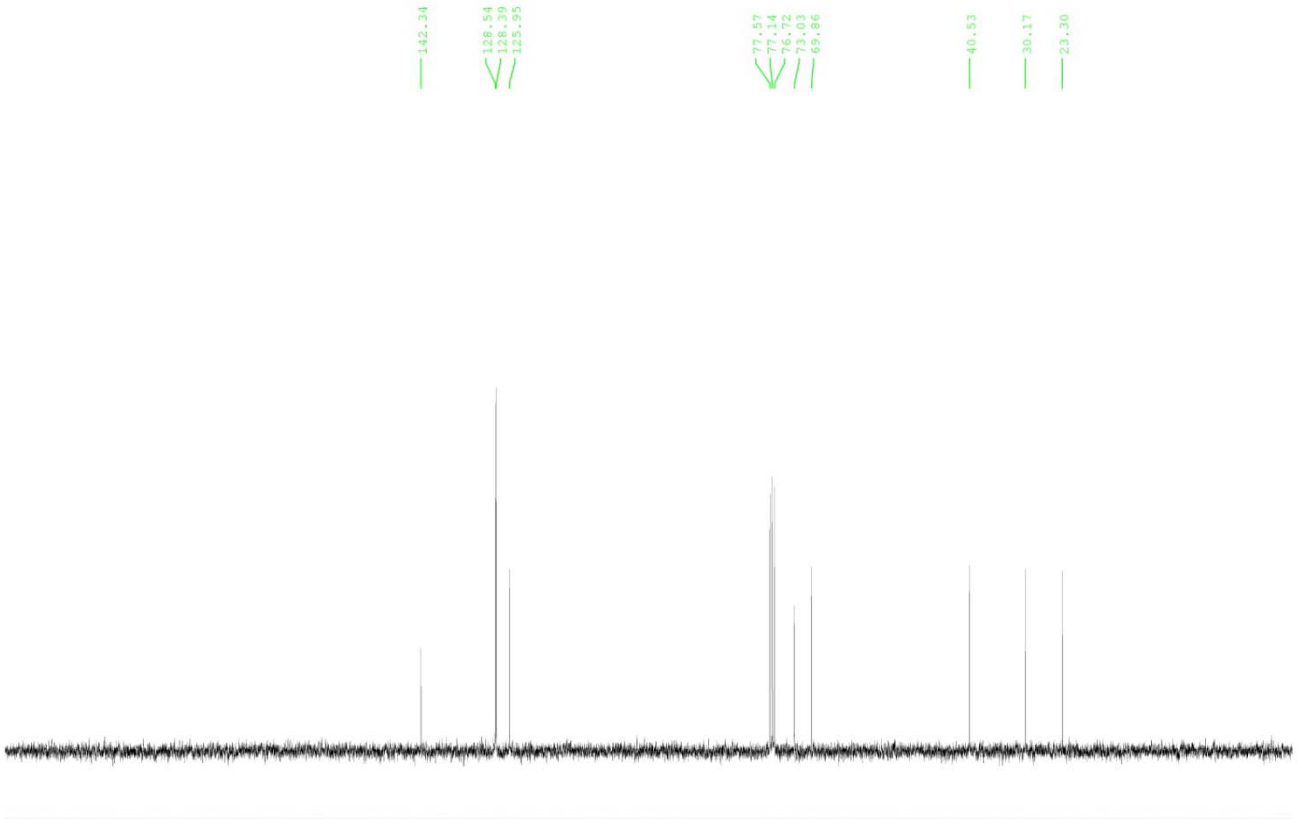


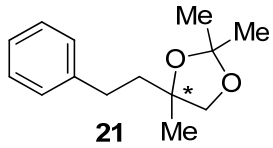
11

^{1}H NMR



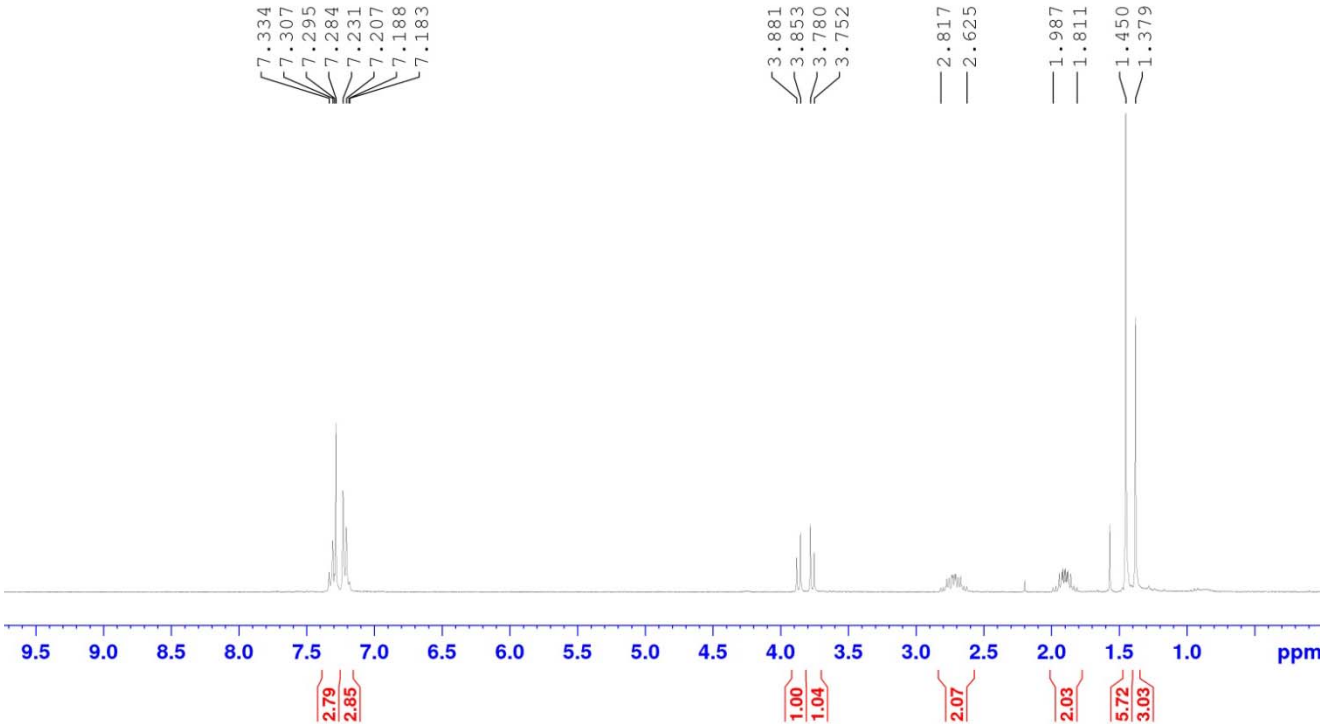
^{13}C NMR



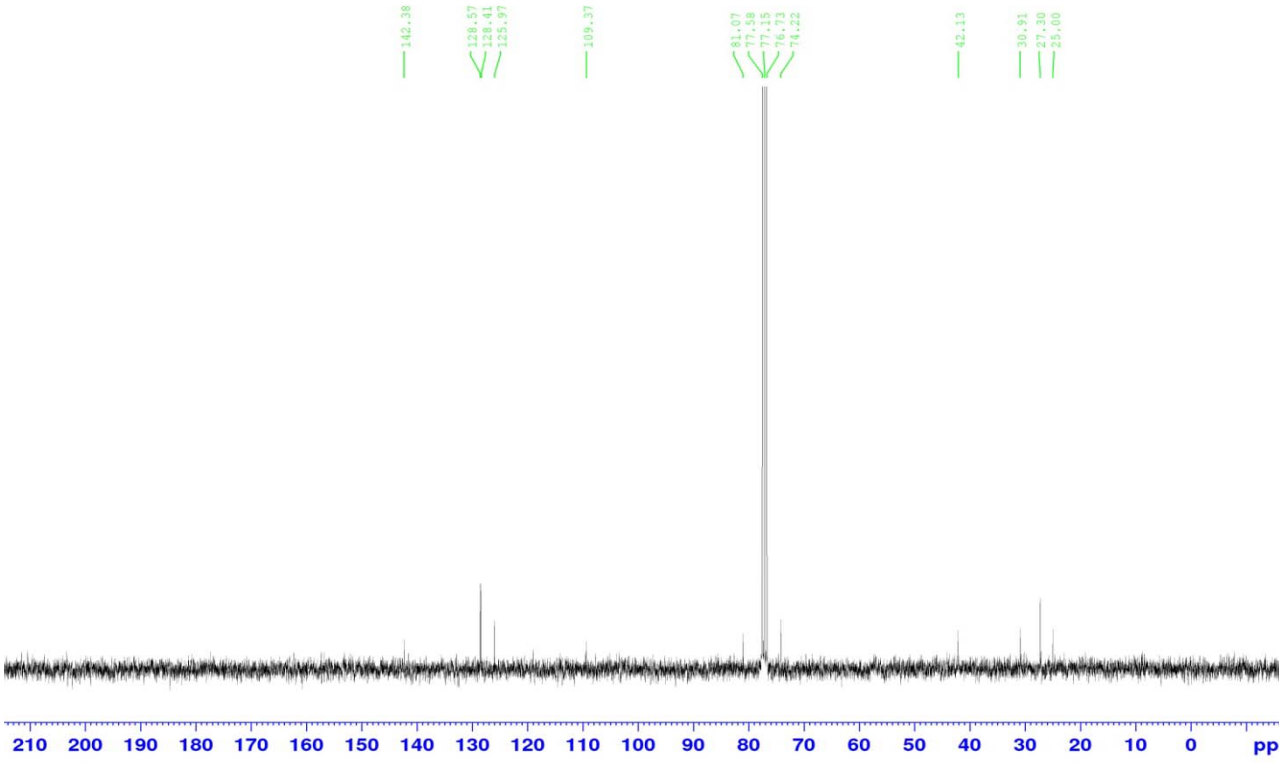


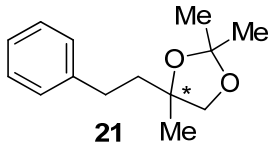
21

^{1}H NMR



^{13}C NMR

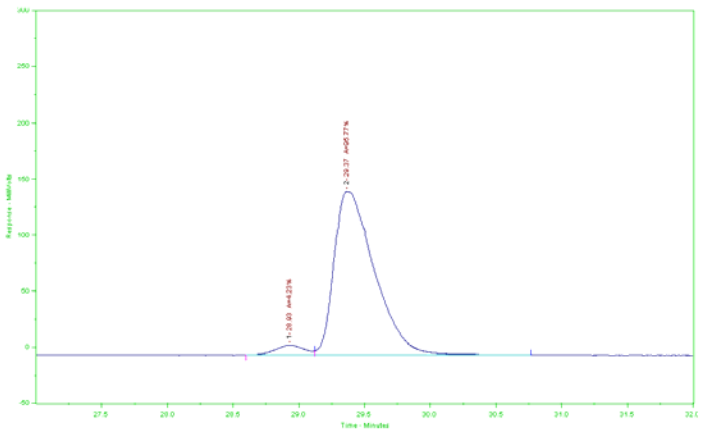




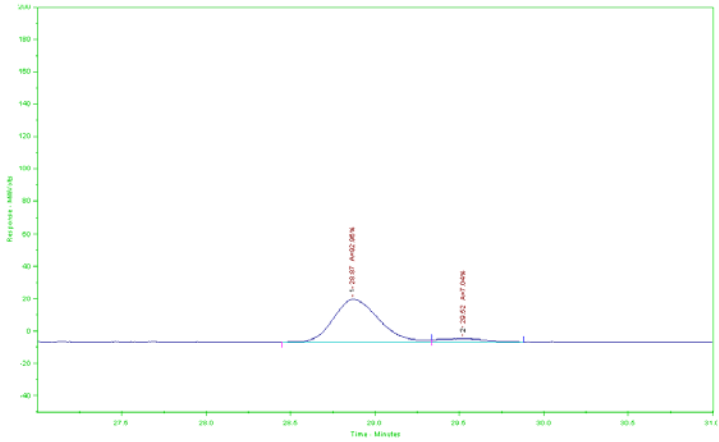
21

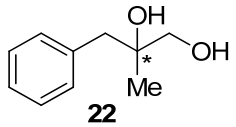
GC traces (CP-Chirasil-DEX CB, 130^0 isoterm)[6]

a) *S:R* = 4:96, acetonide of diol after N-O cleavage of **6j** product obtained in CAHB of **10j** with (*S*,*S*)-L



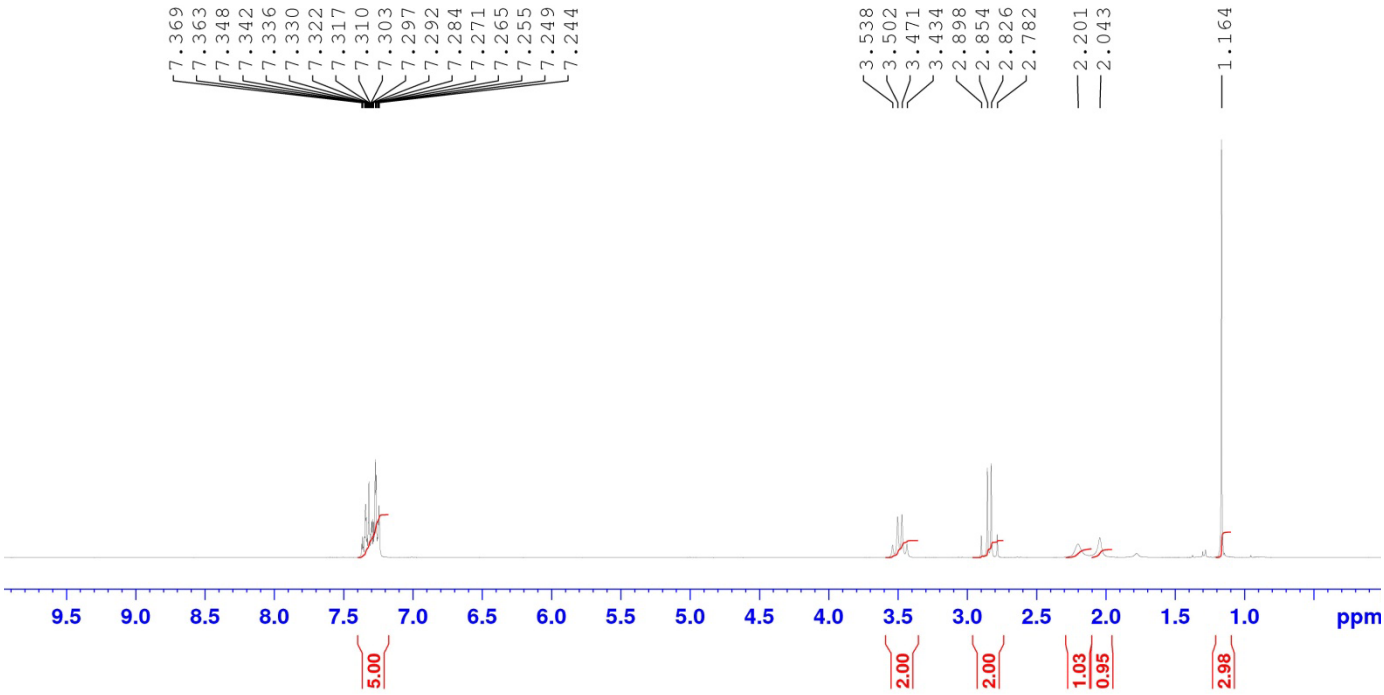
a) *S:R* = 93:7 acetonide of diol after N-O cleavage of **6j** product obtained in CAHB of **10j** with (*R*,*R*)- L



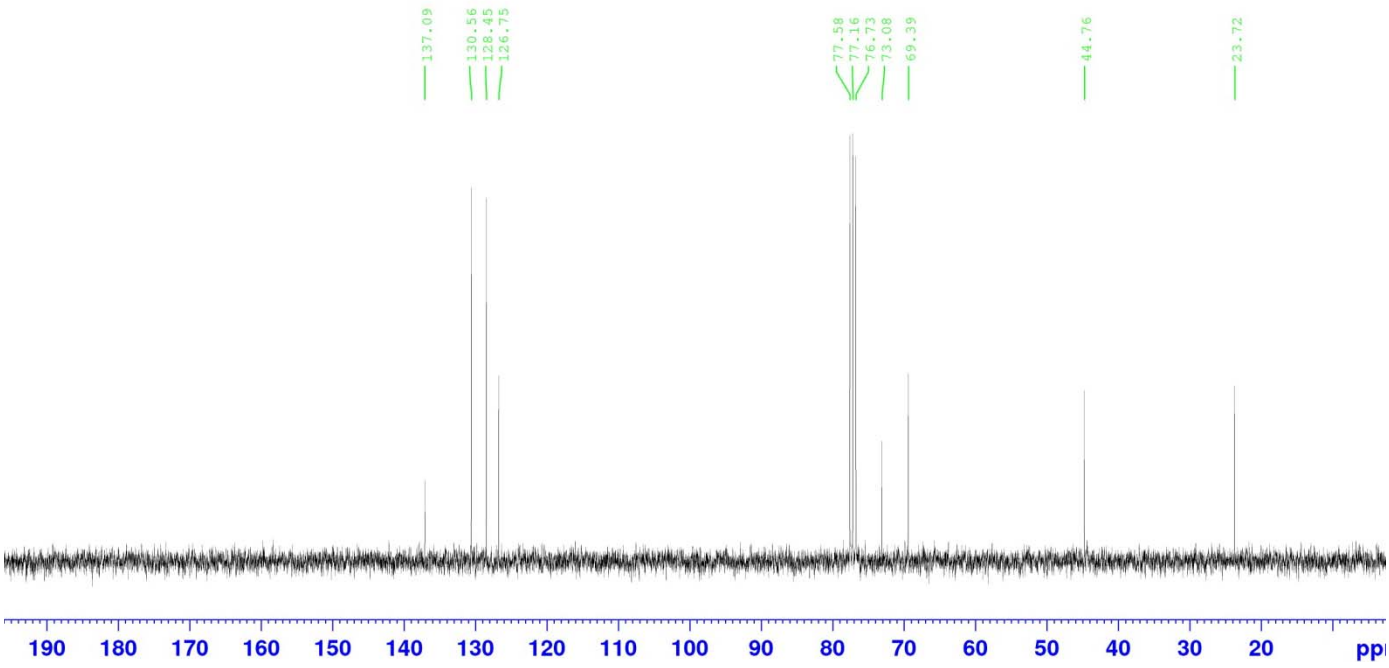


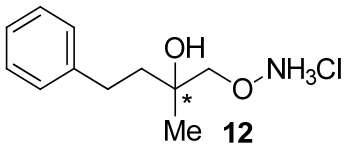
22

^{1}H NMR



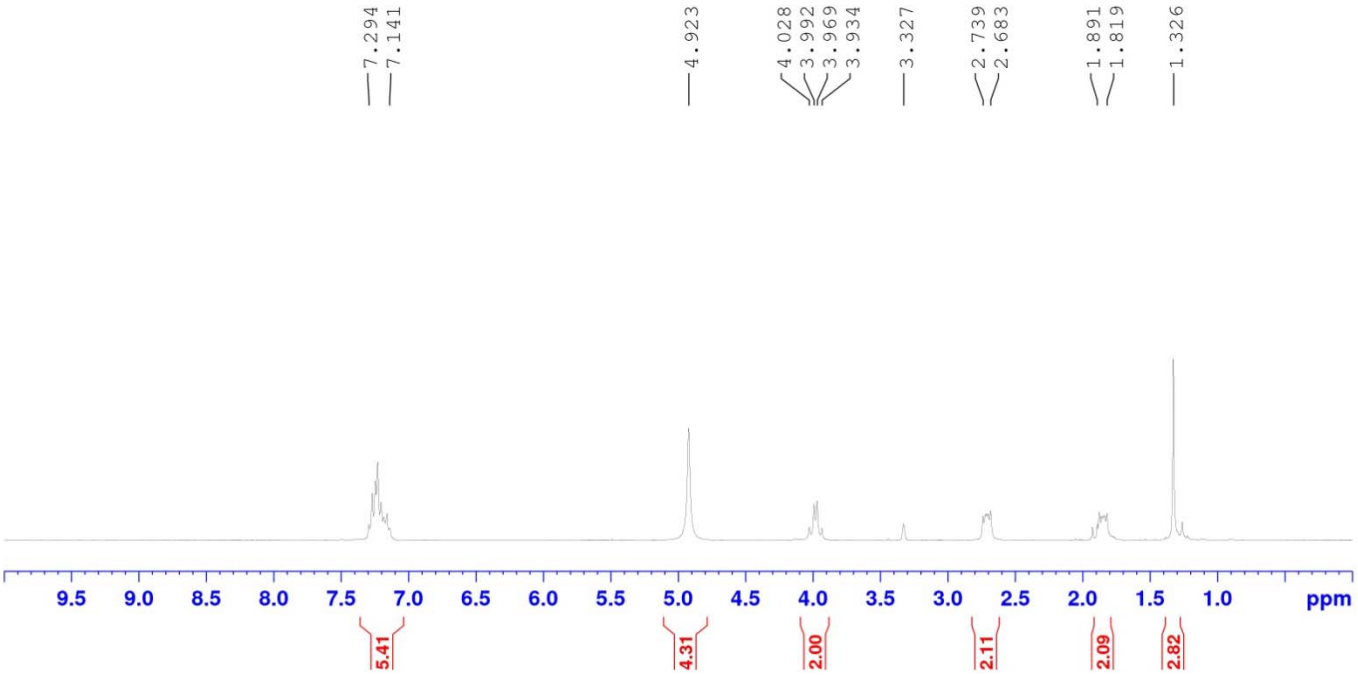
^{13}C NMR



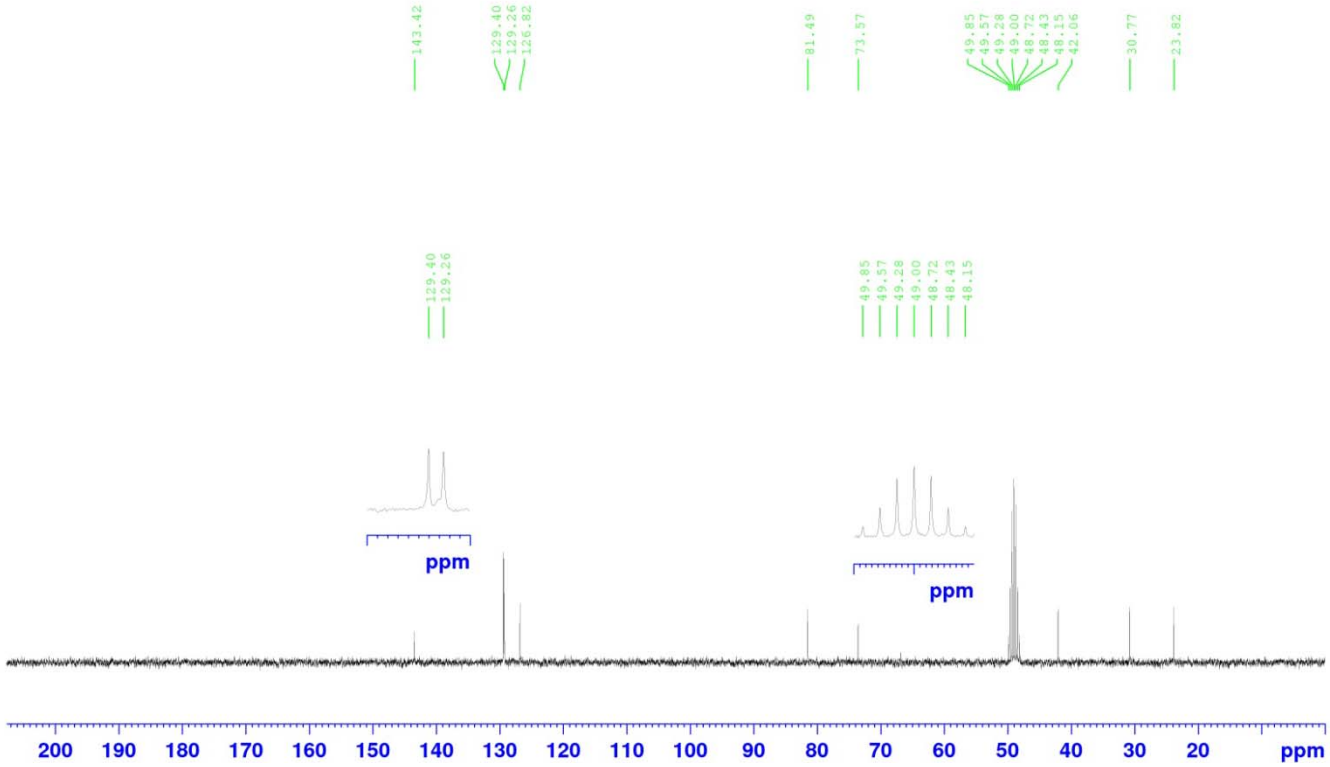


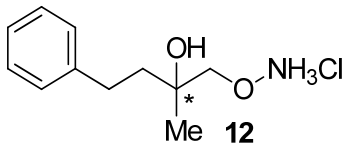
12

^{1}H NMR



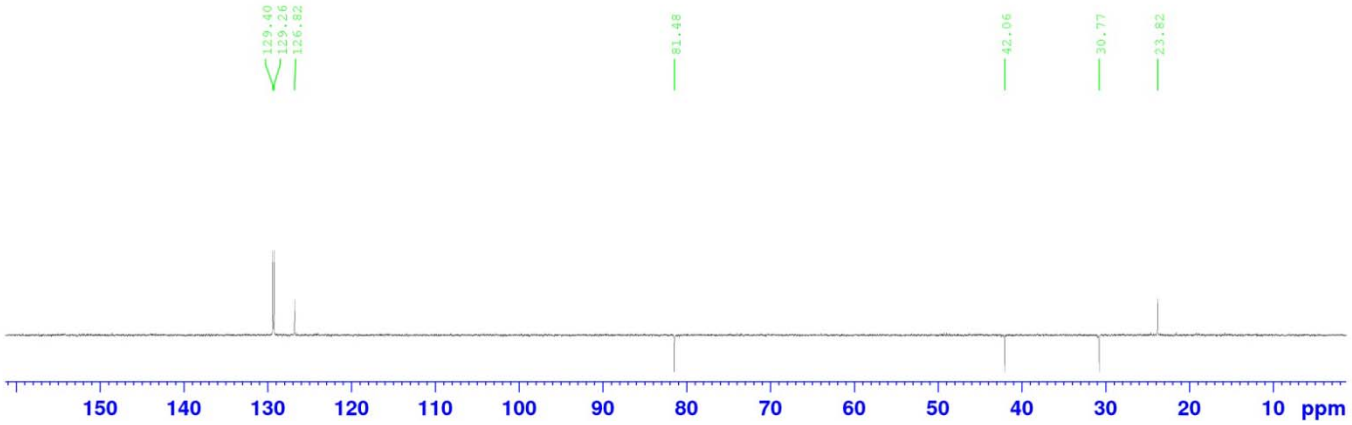
^{13}C NMR



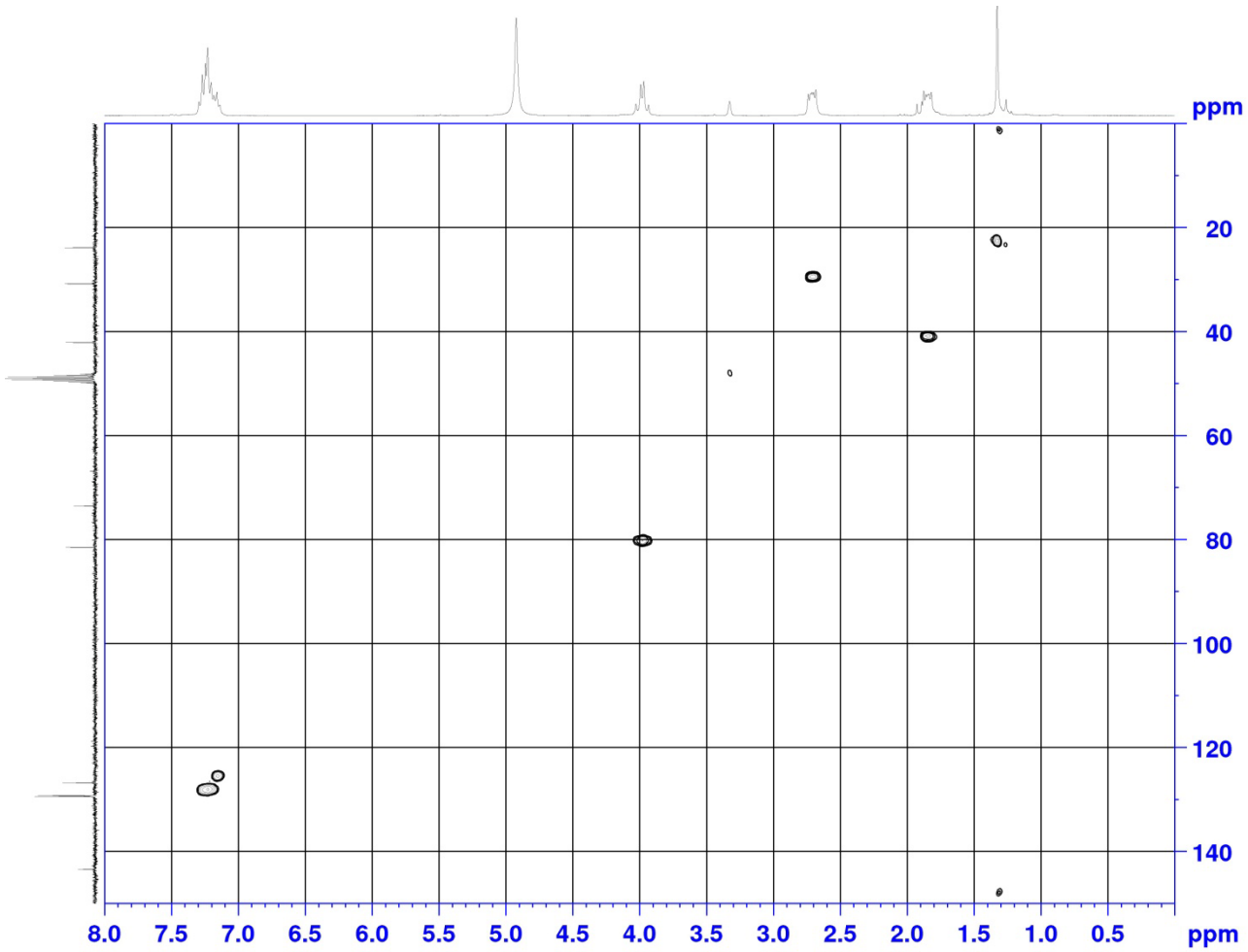


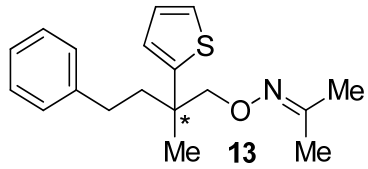
12

^{13}C DEPT 135 NMR



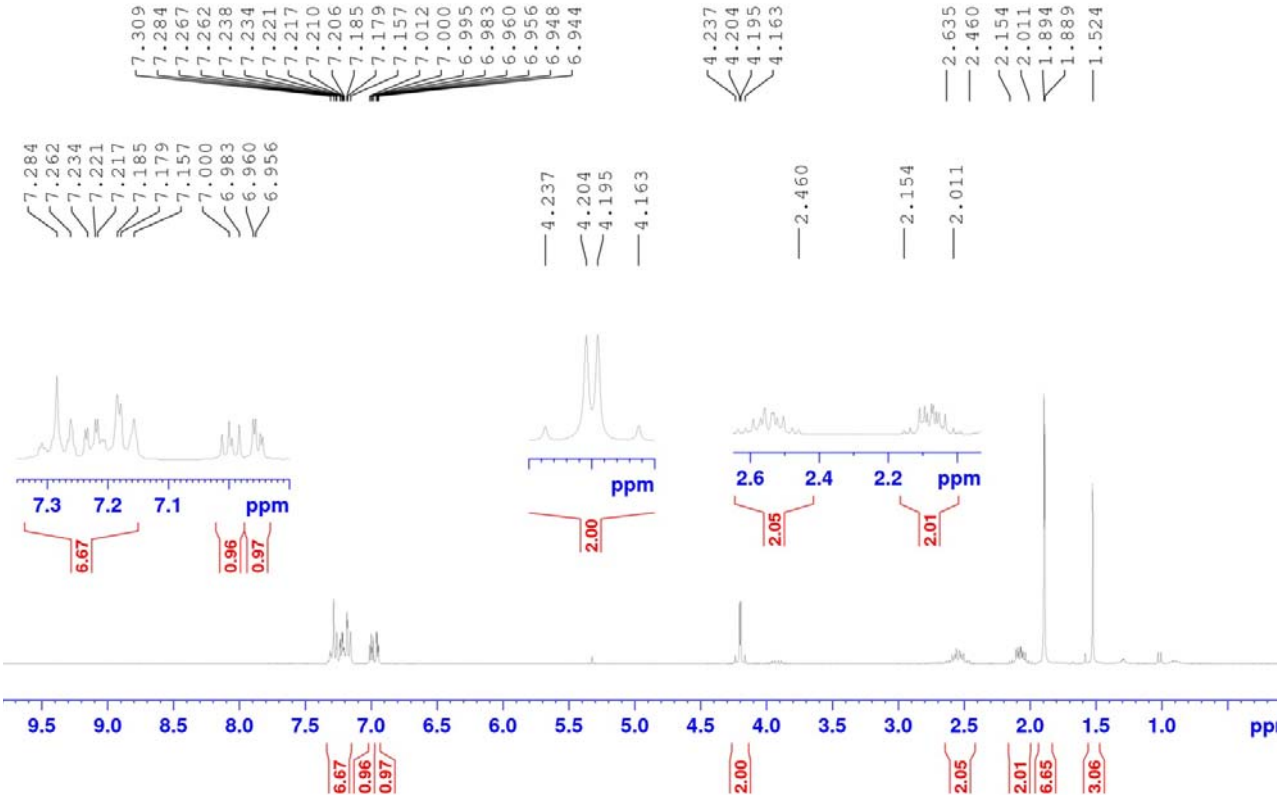
^{1}H- ^{13}C HSQC NMR



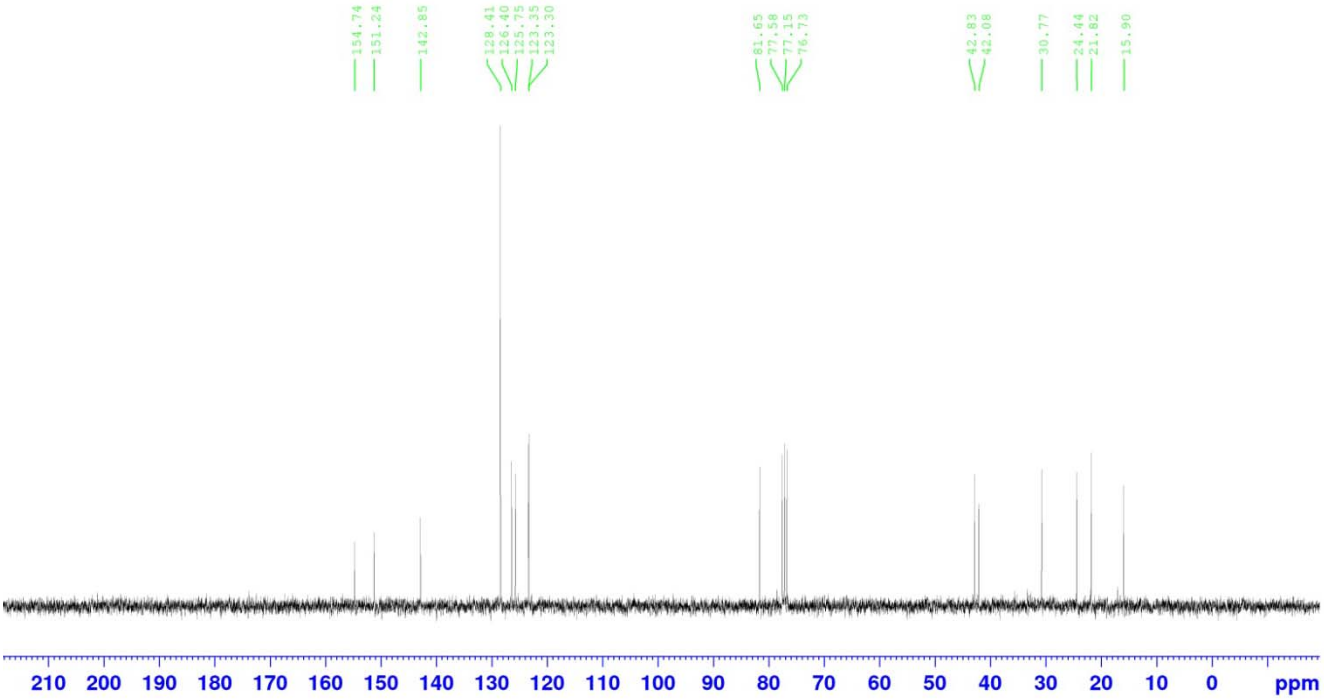


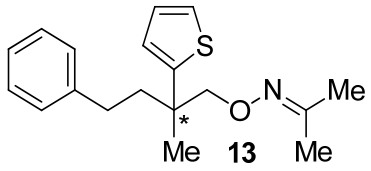
13

^{1}H NMR

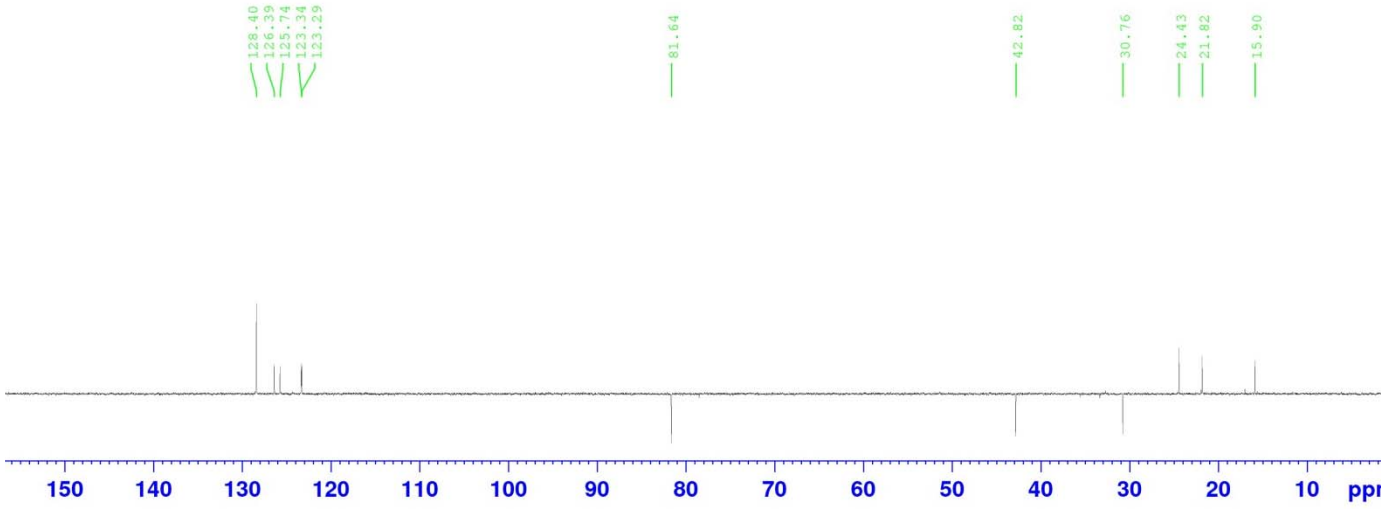


^{13}C NMR

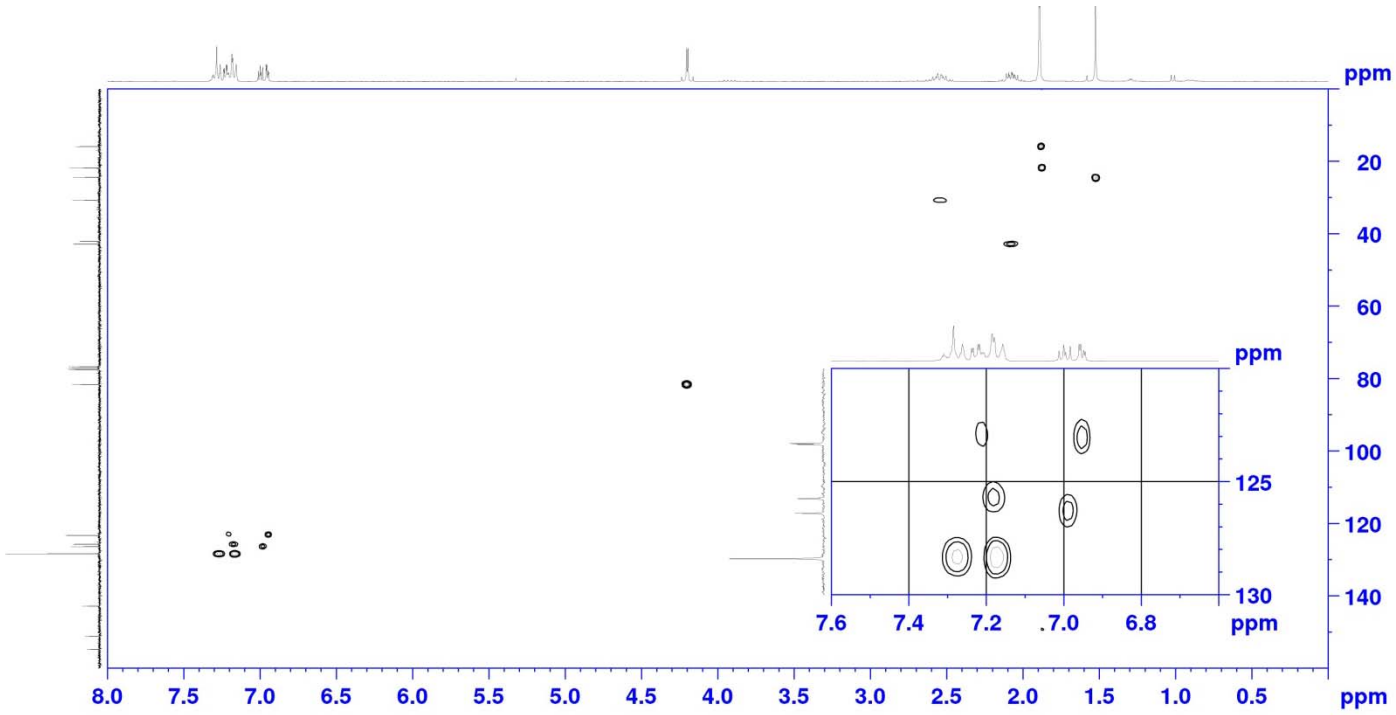


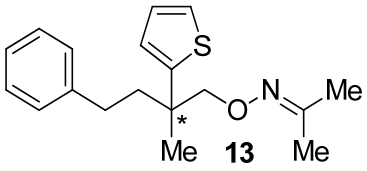


^{13}C DEPT 135 NMR



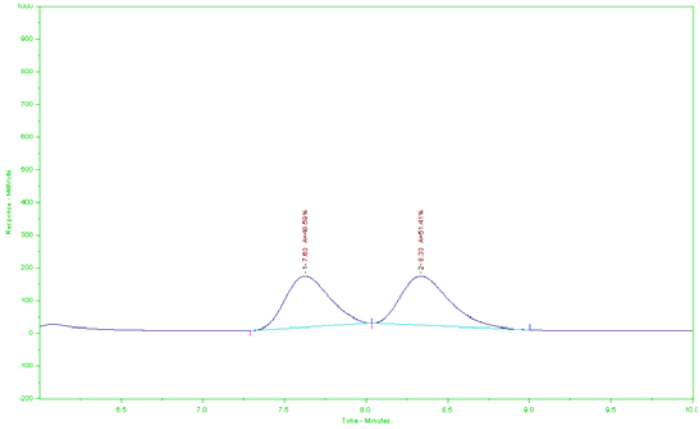
^{1}H-^{13}C HSQC NMR



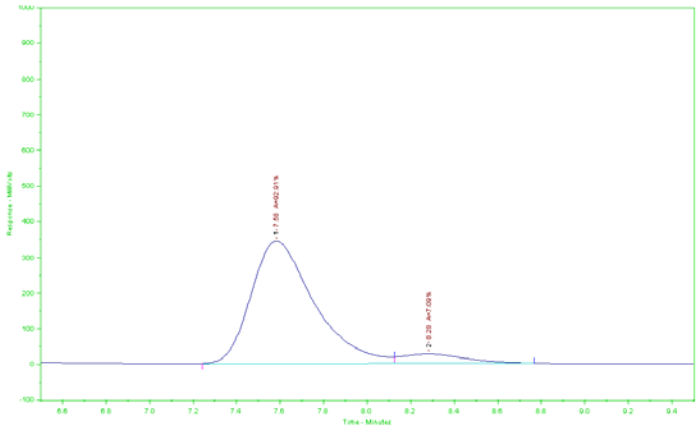


HPLC traces (Chiralpak-AD, 97:3 hexanes:isopropanol @ 1.0 mL/min)

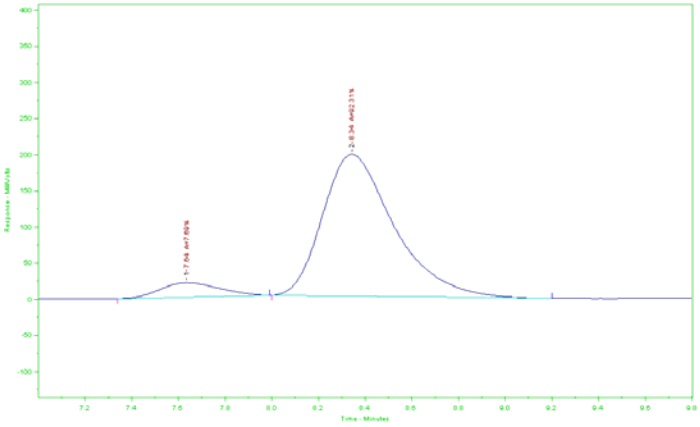
a) racemic mixture



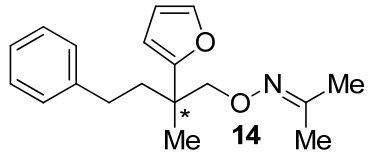
b) *S:R* =93:7, after coupling of thiophene with (*S*)-**7j**

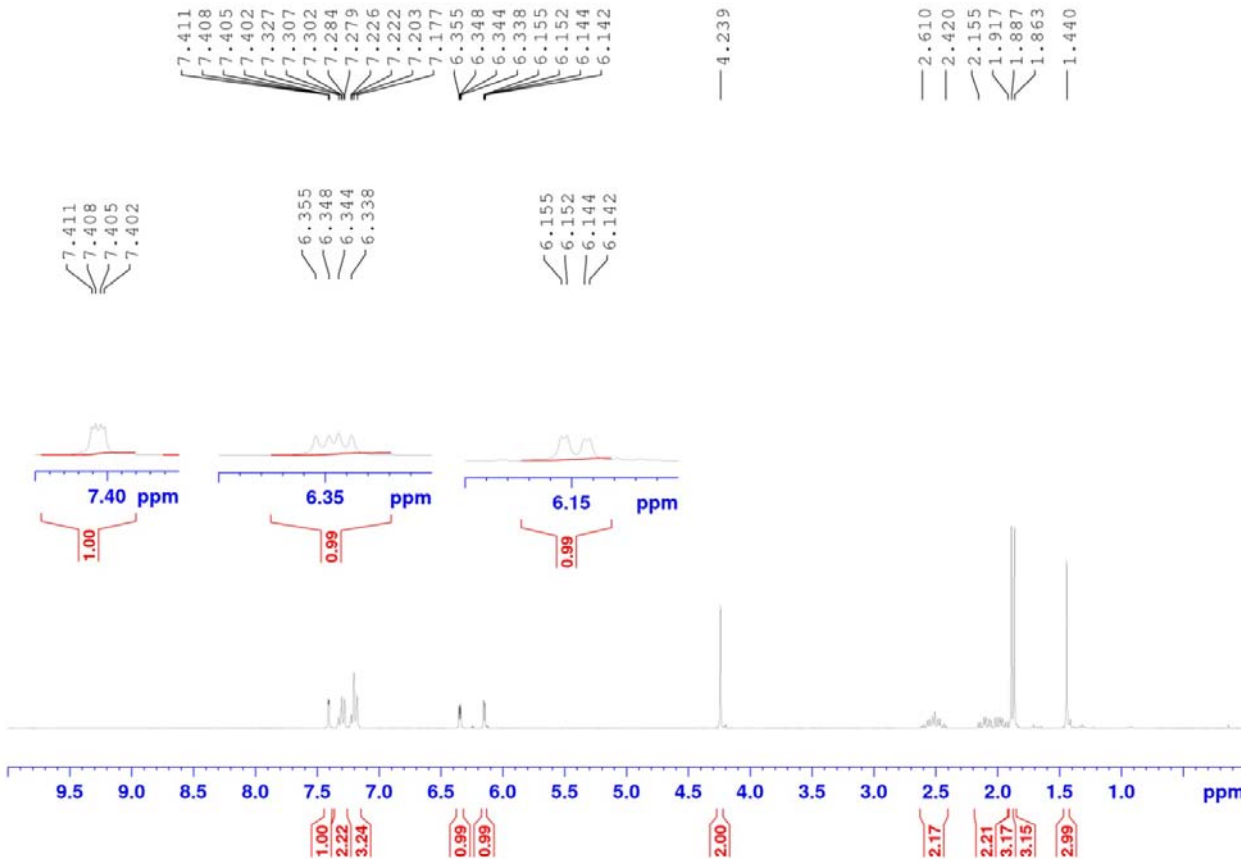


b) *S:R* =7:93, after coupling of thiophene with (*R*)-**7j**

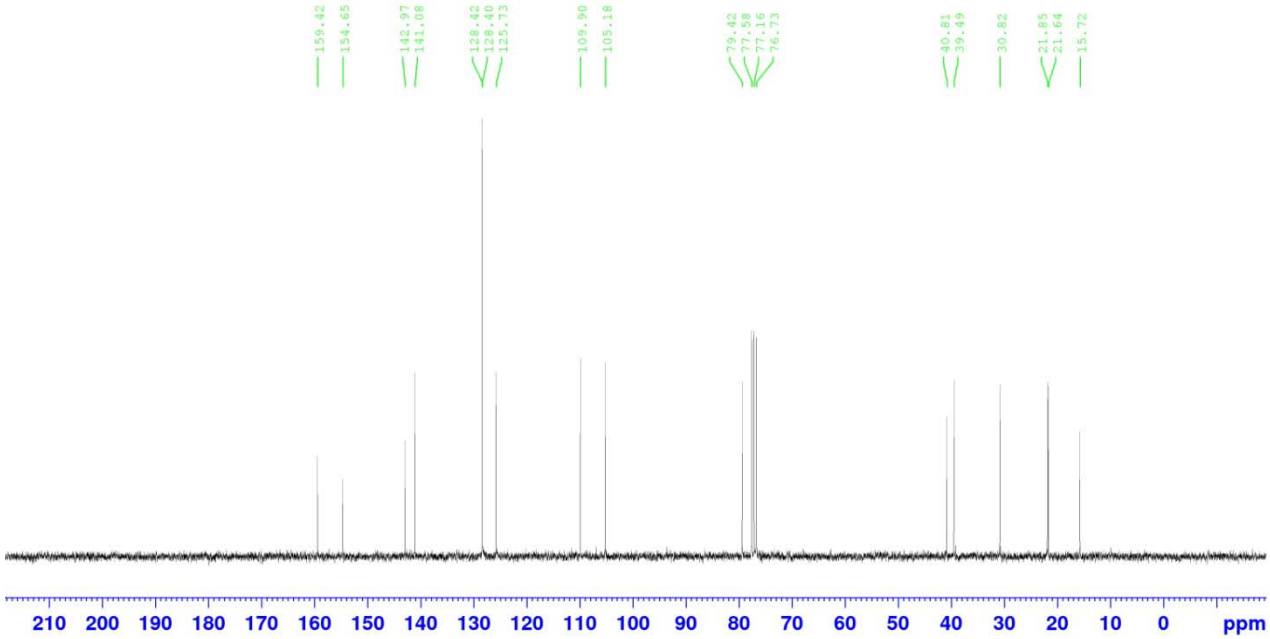


^{1}H NMR

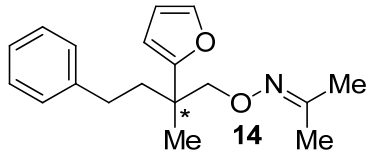


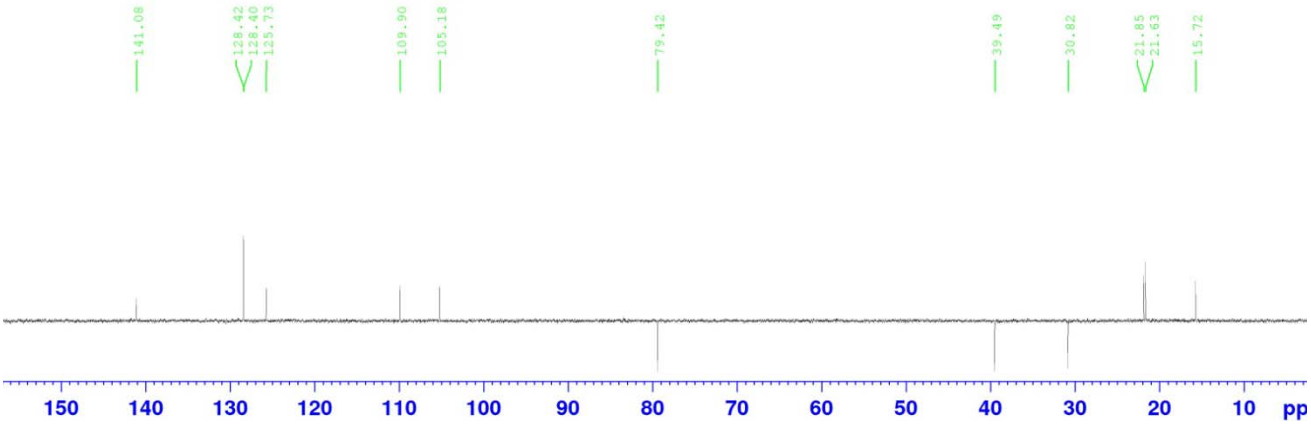


^{13}C NMR

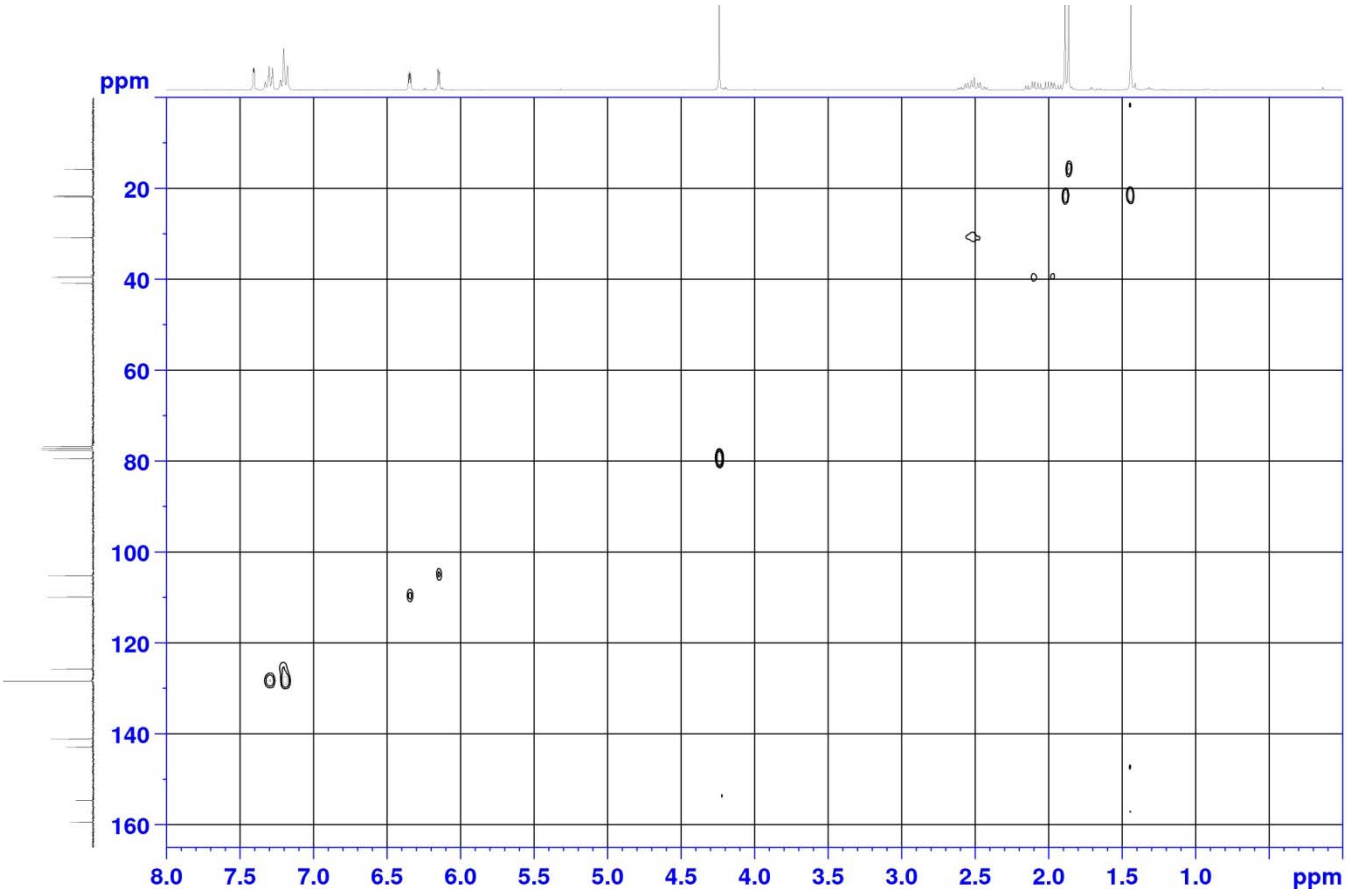


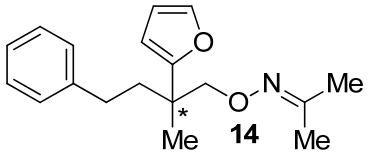
^{13}C DEPT 135 NMR





^{1}H-^{13}C HSQC NMR





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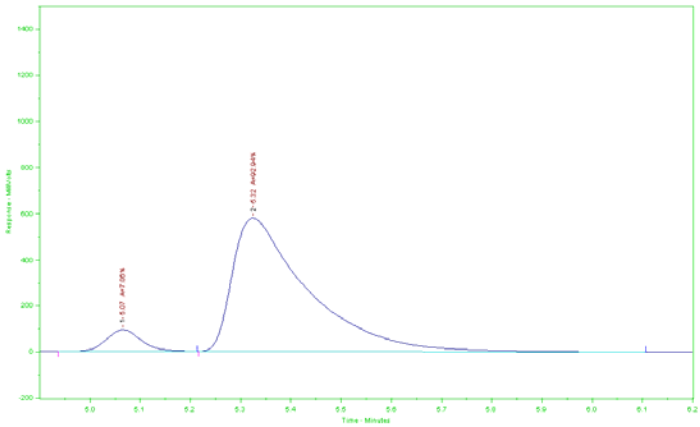
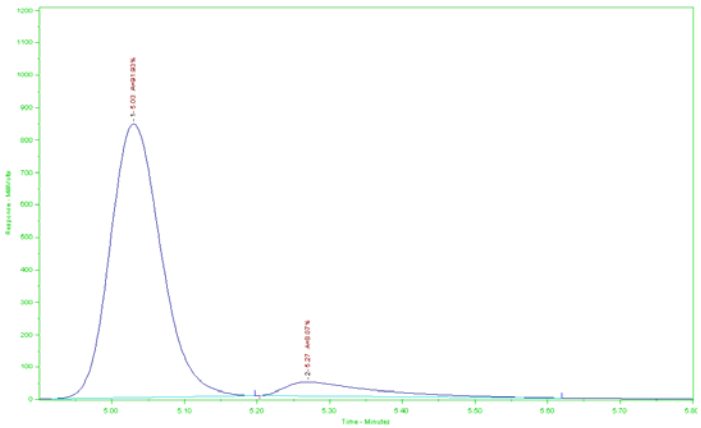
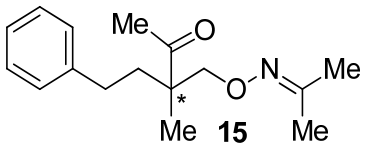
HPLC traces (Chiralpak-AD, 97:3 hexanes:isopropanol @ 1.0 mL/min)

a) *R*:*S* = 7:93 after coupling of furan with (*S*)-**7j**

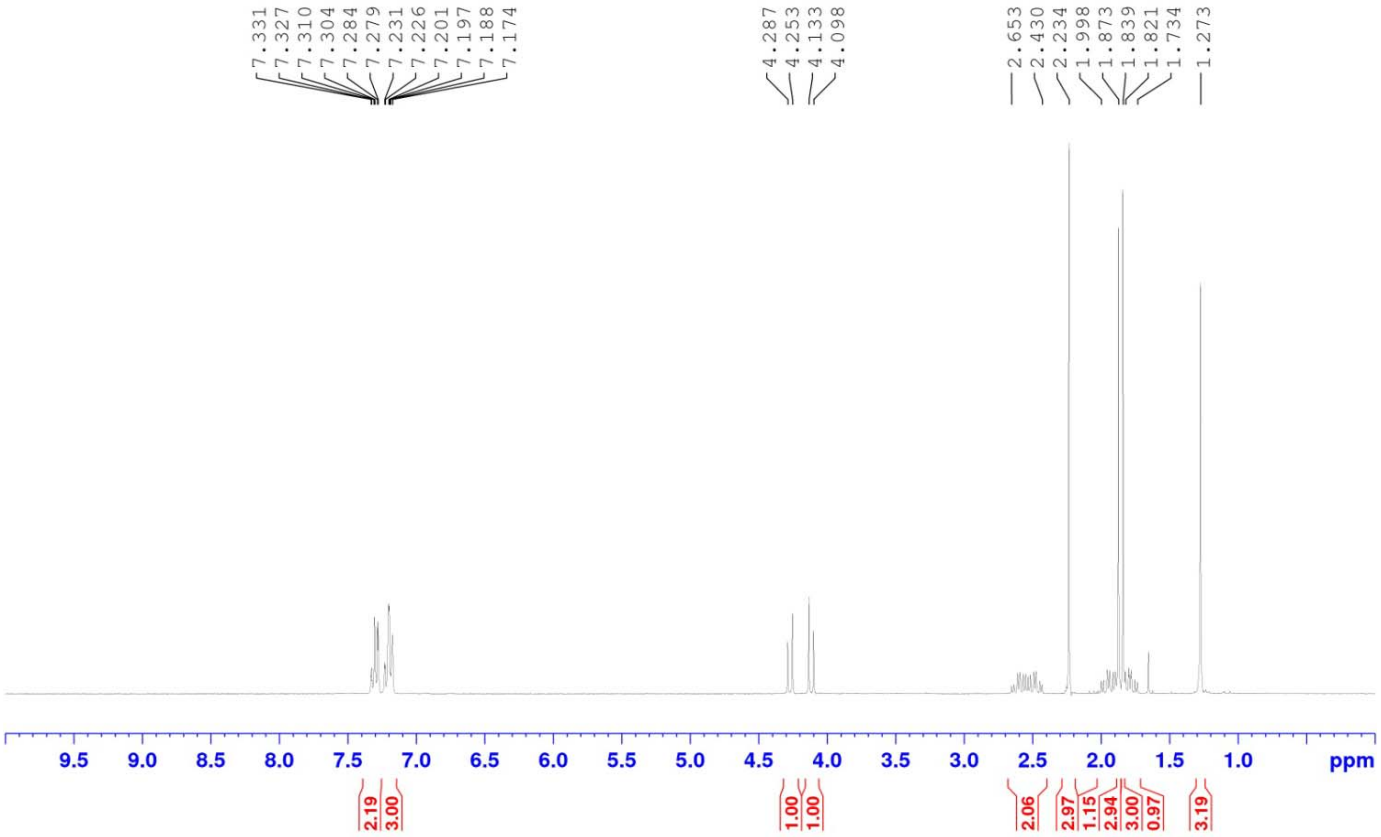


b) *R*:*S* = 92:8 after coupling of furan with (*R*)-**7j**

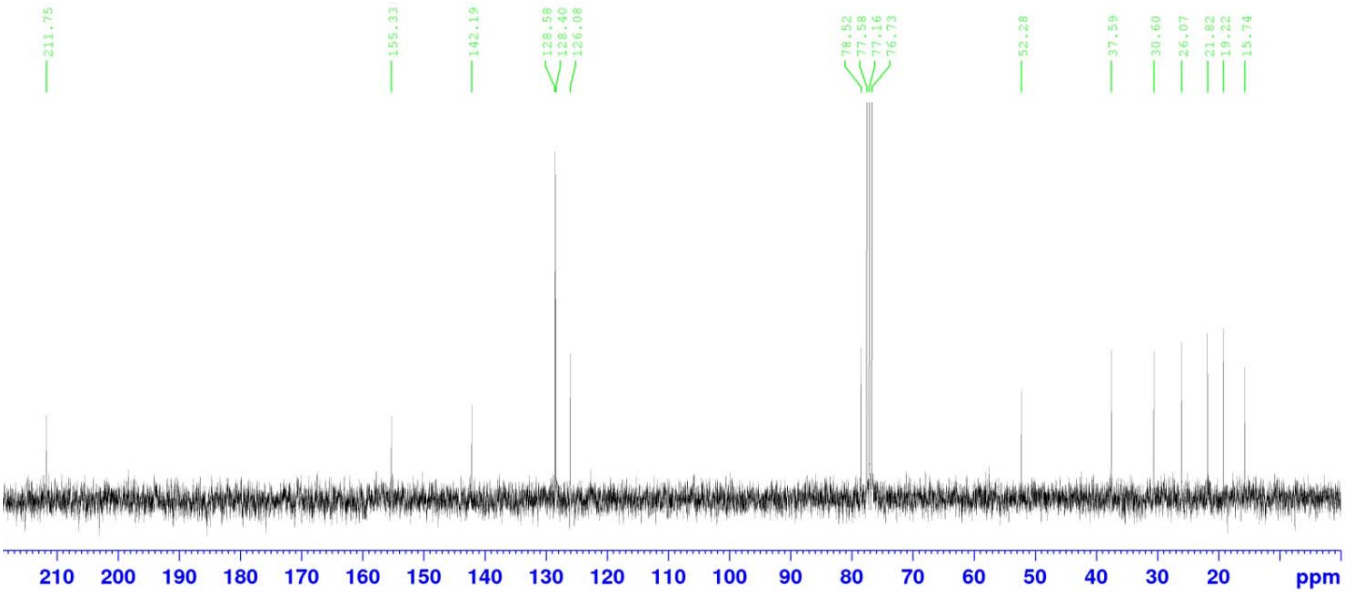


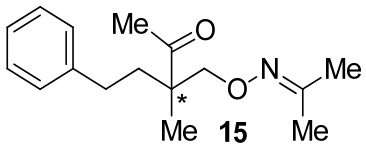


^{1}H NMR



^{13}C NMR





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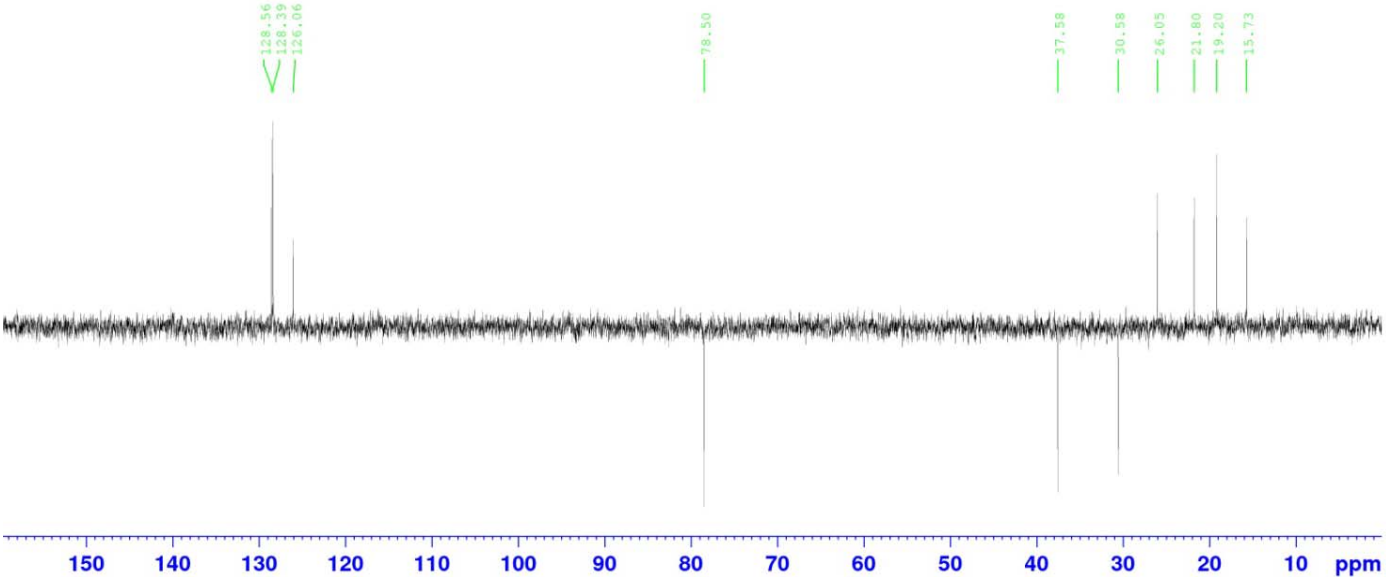
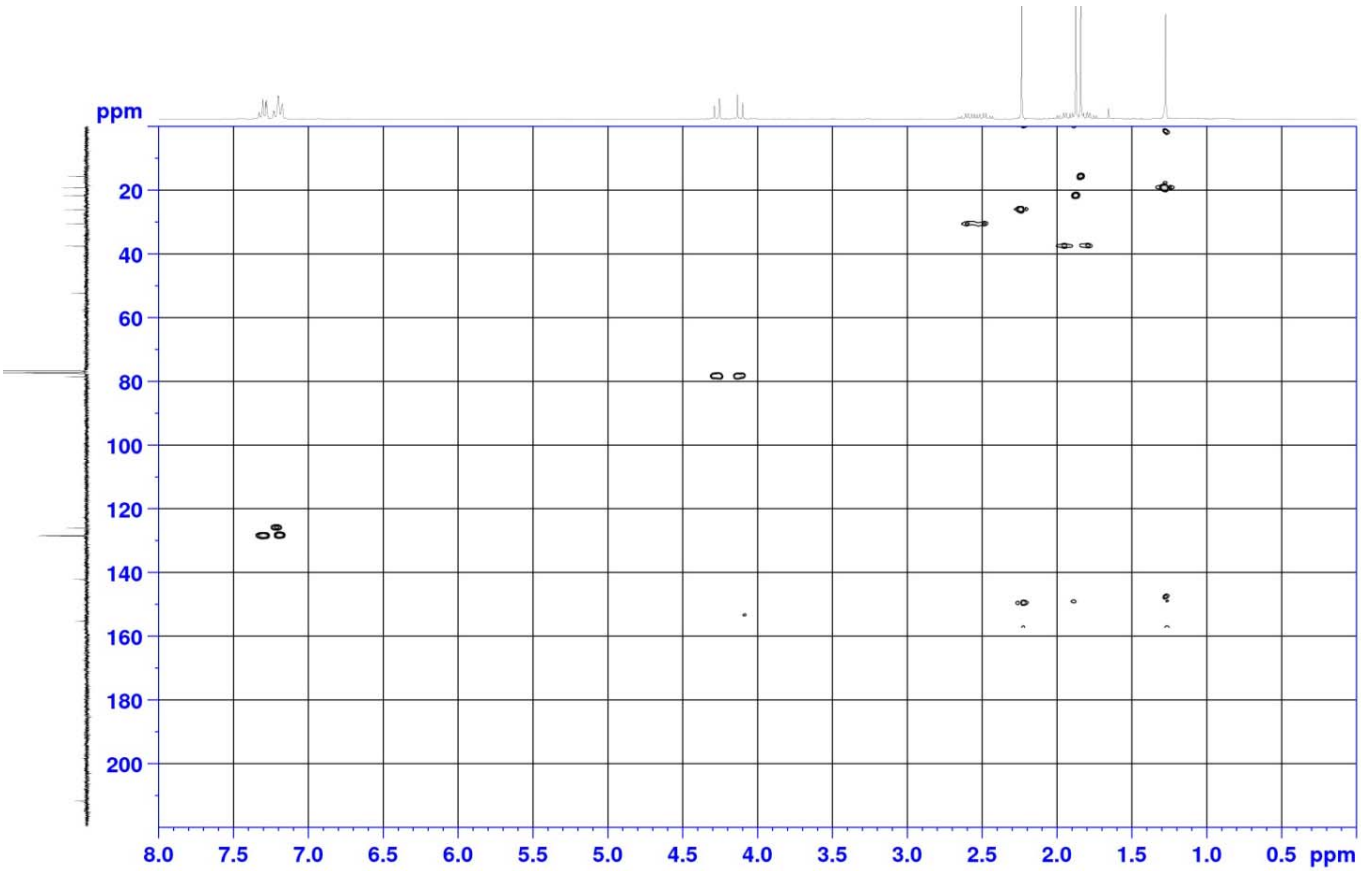
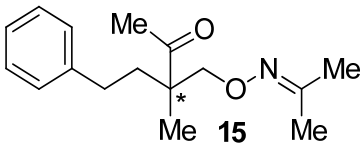
^{13}C DEPT 135 NMR



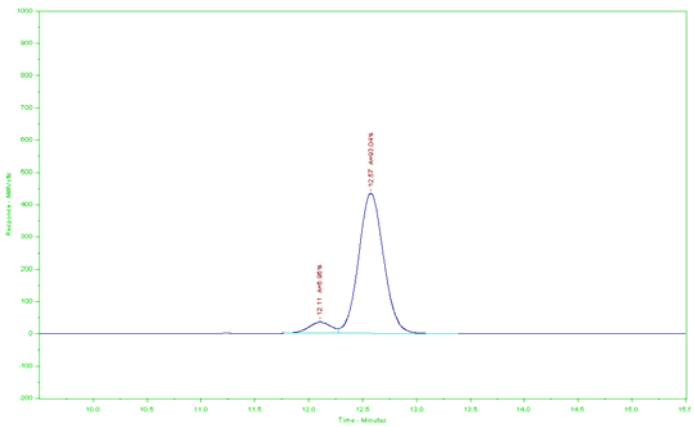
^{1}H- ^{13}C HSQC NMR

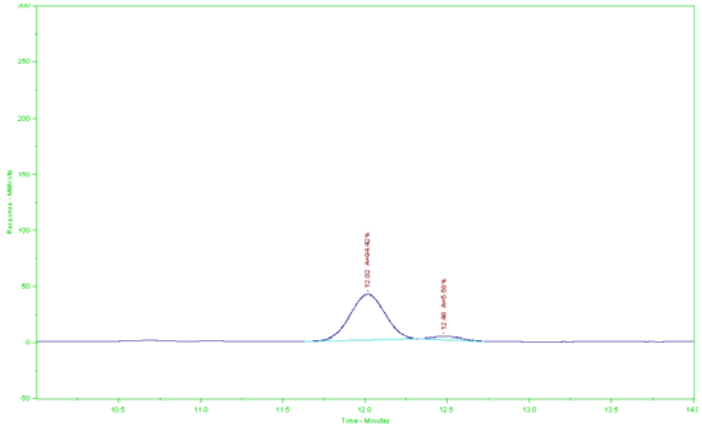


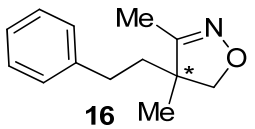


HPLC traces (Chiralpak IC, 90:10 hexanes:isopropanol @ 1.0 mL/min)

a) *R:S = 7:93,* coupling of vinyl ethyl ether with (*S*)-**7j** b) *R:S = 94:6,* coupling of vinyl ethyl ether with (*R*)-**7j**

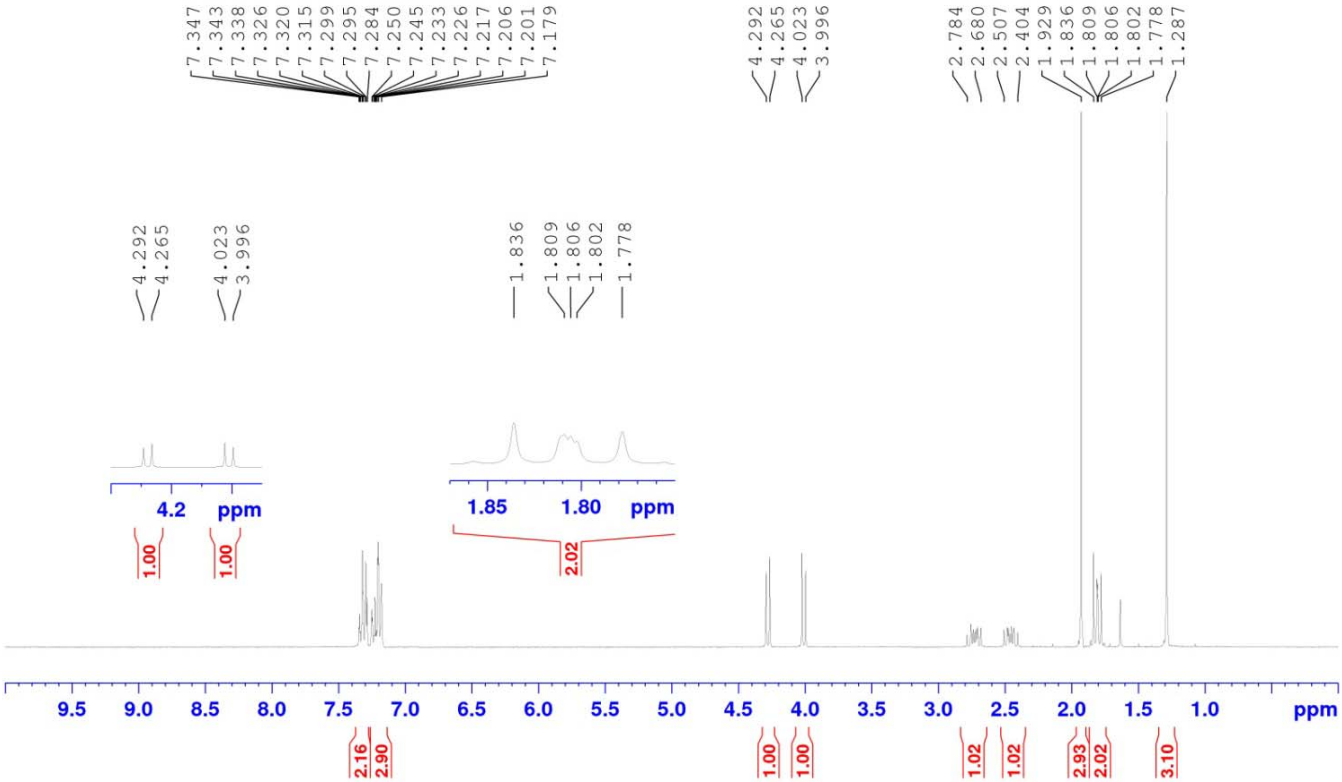




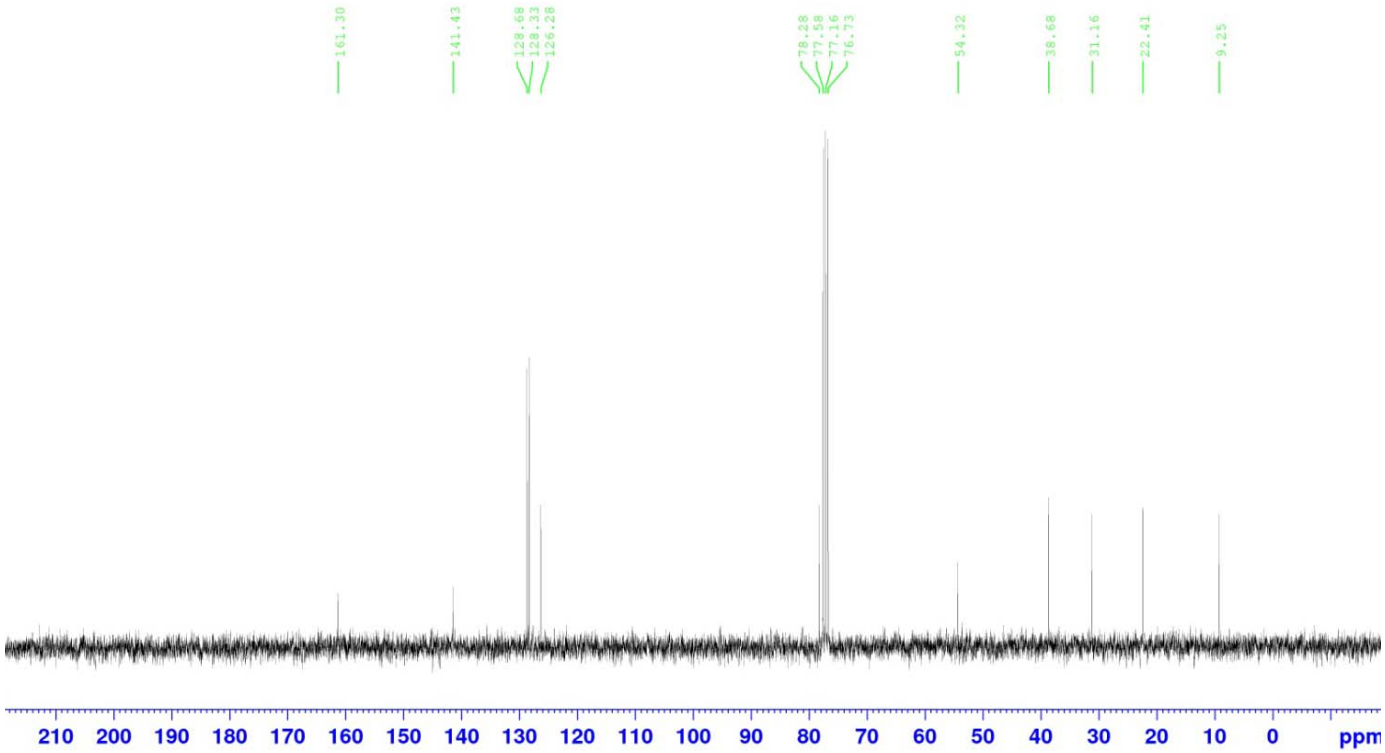


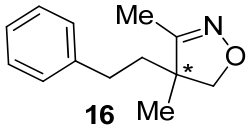
16

^{1}H NMR



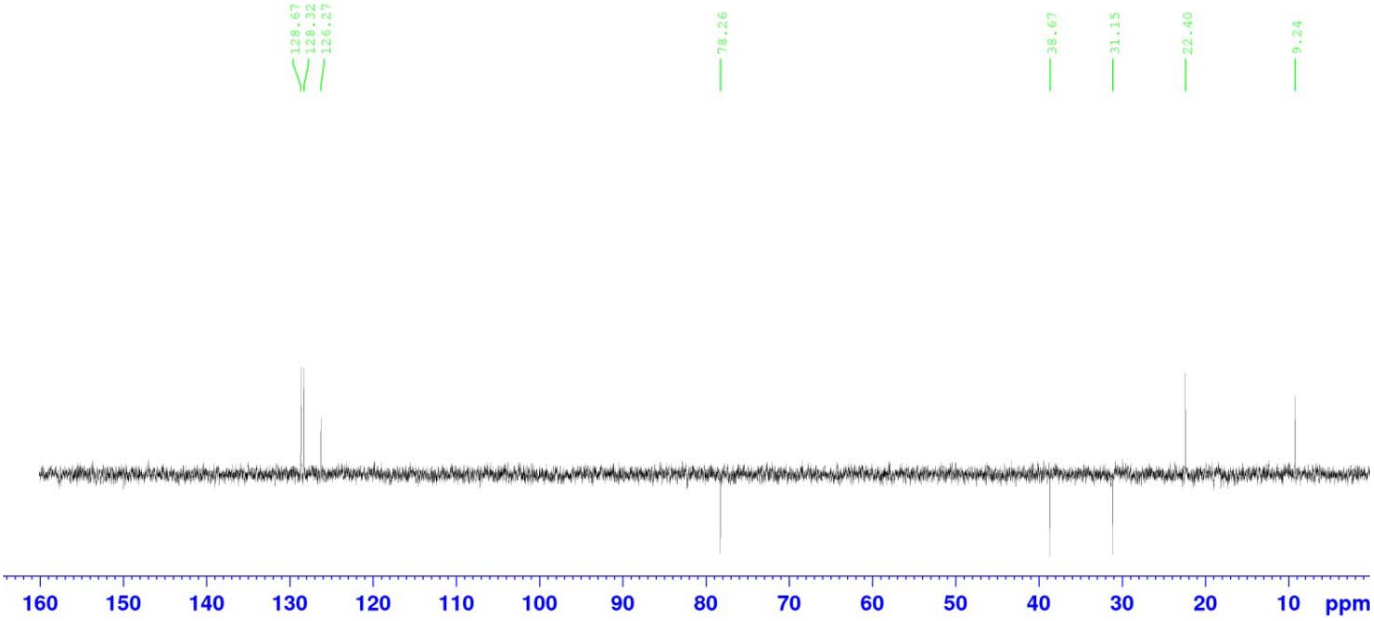
^{13}C NMR



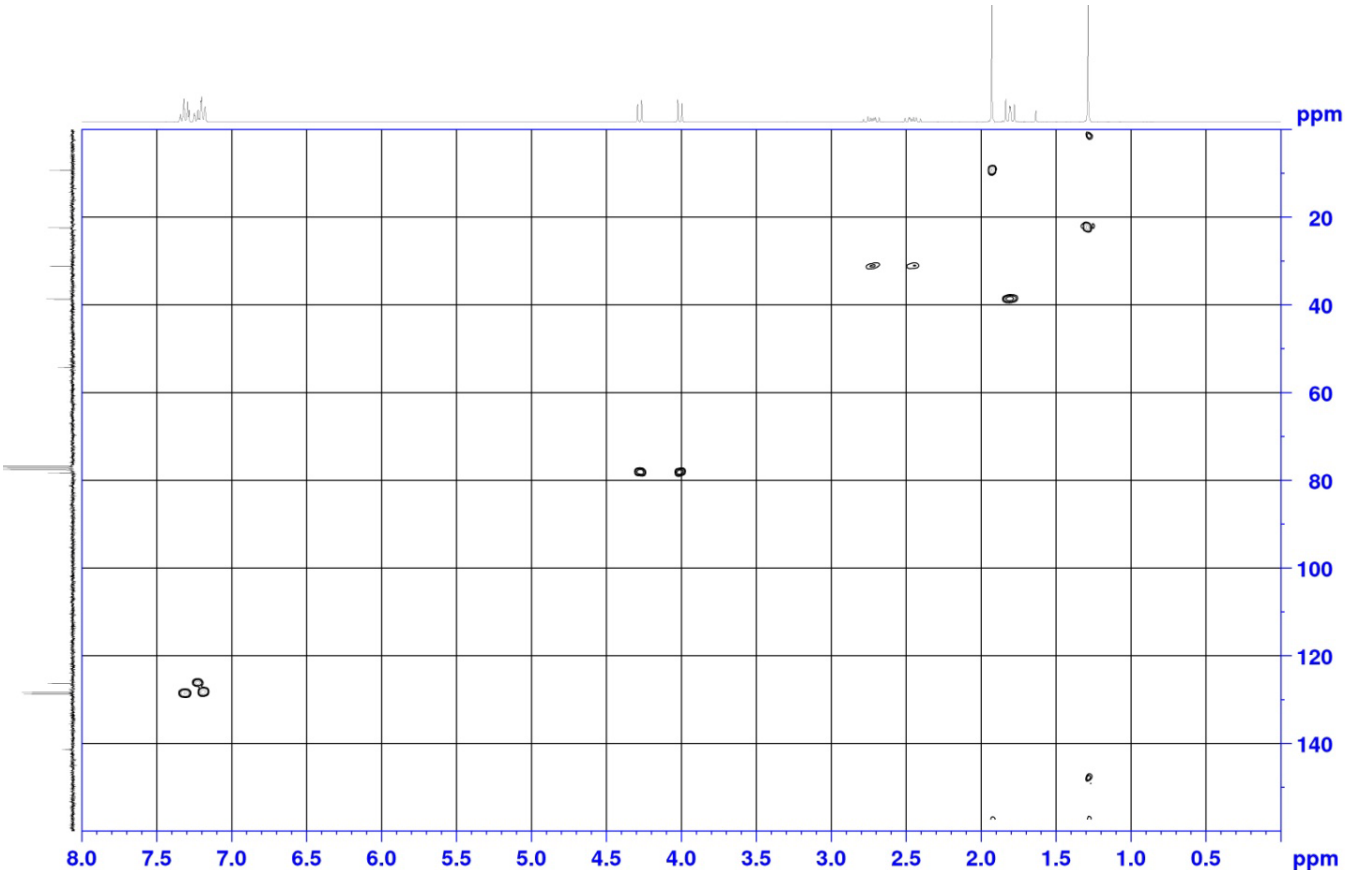


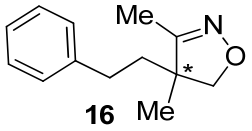
16

^{13}C DEPT NMR



^{1}H- ^{13}C HSQC NMR





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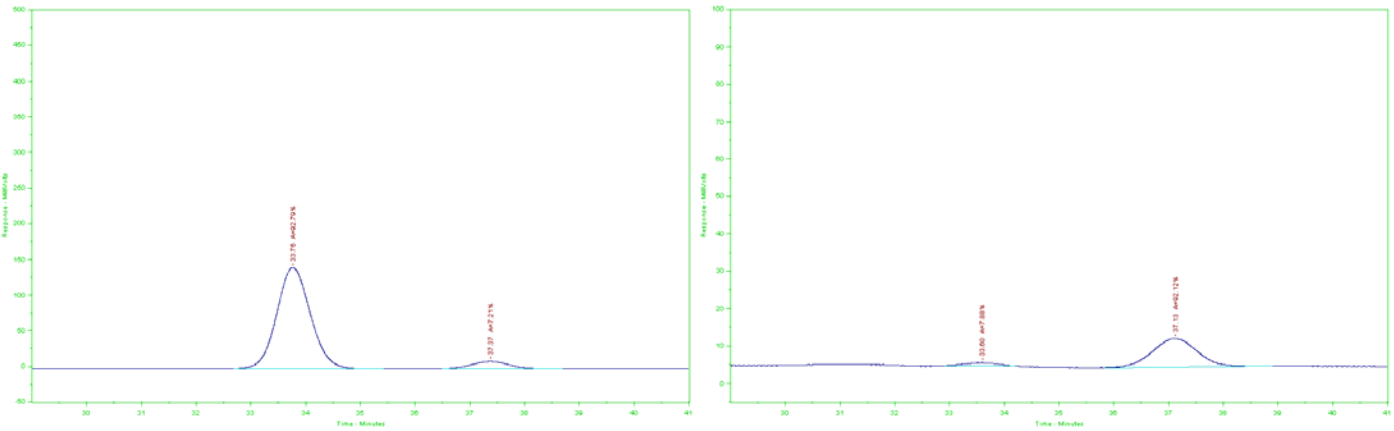
HPLC traces (Chiralpak-IC, 70:30 hexanes:isopropanol @ 1.0 mL/min)

a) *R:S* = 93:7, C=N cleavage and cyclization of (*S*)-**15;** b) *R:S* = 7:93, C=N cleavage and cyclization of (*R*)-**15**



References:

[1] C. C. Browder, F. P. Marmsater, F. G. West, *Org. Lett.,* **2001,** *3*, 3033-3035 (SI).
[2] L. W. Ye, X. Han, X. L. Sun, Y. Tang, *Tetrahedron*, **2008**, *7*, 1487-1493(SI).
[3] A. Erkkila, P. M. Pihko, *Eur. J. Org. Chem.* **2007**, 4205–4216.
[4] K. Guo, X. Chen, M. Guan, Y. Zhao, *Org. Lett.* **2015**, *17*, 1802−1805 (SI).
[5] M. Szostak, M. Spain, D. Procter, *J. Chem. Commun*. **2011**, *47*, 10254 (SI).
[6] I. Osprian, W. M. Kroutil, M. Mischitz, K. Faber, *Tetrahedron: Asymmetry*, **1997**, *8*, 65-71.
[7] V. F. Stephen, L. E. Ernest, *J. Org. Chem*. **1985**, *50*, 3402.
[8] A. Bonet, M. Odachowski, D. Leonori, S. Essafi, V. K. Aggarwal, *Nat. Chem*. **2014**, *6*, 584−589 (SI).